RUBBER CHEMISTRY AND TECHNOLOGY

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RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published five times per year under the supervision of the Editor, representing the Division of Rubber Chemistry of the American Chemical Society. One object of the publication is to render available in convenient form under one cover important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances. Another object is to publish timely reviews.

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CARROLL CAMPBELL DAVIS

1888–1957

By the death of C. C. Davis, RUBBER CHEMISTRY AND TECHNOLOGY has lost its editor, the world of rubber literature has lost its most prominent authority, and all of us have lost a warm personal friend.

Carroll Campbell Davis, affectionately known as "C.C.," was born in Boston in 1888 and lived there all of his life. After graduating from Dartmouth, he received a degree in Chemical Engineering at Massachusetts Institute of Technology. For forty-two years he was an employee of the Boston Woven Hose and Rubber Company and was their Chief Chemist when he retired a little over a year ago.

His life had two parallel parts, his daily work in the plant of a rubber manufacturer and his outstanding devotion to the field of rubber literature. In both of these areas he was exceedingly successful, although it was in the latter that he attained international renown.

As a result of his industrial work, his name is perpetually associated with the universal aging test—the Bierer-Davis Oxygen Bomb. In the early 1920's there was an intense need for appraising the potential life of a rubber compound. There were only two methods at that time of anticipating the life of a rubber article, natural aging at room temperature and the Geer oven test. This latter was new and rubber technologists had used it only to a limited extent. It was universally conceded that much of the deterioration of rubber was due to oxidation although the effects of heat and ozone were well recognized. Bierer and Davis conceived the idea that the way to accelerate the action was to increase the concentration of oxygen by means of pressure and at an elevated temperature. In retrospect it was a logical and simple extension of the Geer oven test, but it was a revolutionary step. This large increase in the concentration of oxygen profoundly increased the deterioration of rubber and it became possible to predict by a quick test the behavior of many rubber articles in service.

The development of this tool for the rubber industry was indeed timely. The use of organic vulcanization accelerators and antioxidants was coming to the fore, although there had not been universal adoption. The oxygen bomb test provided a rapid appraisal of compounding techniques and combinations with such dependence that the quality of rubber compounds increased at an astounding rate in the next decade. The economic value of this test to the consuming public was incalculable. Three papers on the subject appeared within a few years.

The value of other portions of Carroll Davis's work in the rubber manufacturing industry cannot be estimated, although we all know of its high quality and can be sure that it was translated into the reputation and profits of his employer.

It is difficult to decide whether the interest of "C.C." in rubber literature was his vocation or avocation. In any event, it was a major portion of his life.

In 1925 he became the editor of the Rubber Section of *Chemical Abstracts*, a position which he continued to hold for 32 years. With the complete coverage of literature by this periodical, he probably knew at first hand practically every-

thing published on the subject of rubber. His operation of this section of *Chemical Abstracts* was a model for others in a similar position in other branches of chemistry.

In 1928 the Rubber Division of the American Chemical Society embarked on an ambitious program. In order to fill a long felt need of its members, it was decided that the important articles on various phases of rubber chemistry and technology be published in convenient form. And so the periodical "RUBBER CHEMISTRY AND TECHNOLOGY" began. There was obviously only one choice for the editorship, and C. C. Davis accepted. He held this position from its inception until his death, a period of 29 years. During this time the publication became the handbook of rubber technologists not only in this country but wherever the English language is read.

On the surface, the publication of R. C. & T. may have seemed an easy task. The average reader has no conception, I am sure, of the hours of labor and thought involved in this work. Obviously, it could not be a simple compilation of articles appearing in the world literature. Because of limited funds and space, the articles "C.C." selected for publication were but a fraction of those available. They were chosen with much discrimination. "C.C." depended not only on his own unerring judgment in their selection, but corresponded extensively with scientists and technologists over all the world in attempting to confirm his opinions. Many letters were written at times before a single paper was selected for inclusion. The quality of these decisions was so well recognized that it became a signal honor for an author to have his article in RUBBER CHEMISTRY AND TECHNOLOGY.

Many of the papers were translated from foreign languages. Carroll Davis had a deep understanding of several languages and he made many of the translations himself. He was a perfectionist in the use of language, with a keen appreciation of the subtle distinction between alternative words, and this is evident in all his writing. One of his major tasks was the conversion of translations into clean-cut idiomatic English which expressed most exactly the ideas of the author. Few of the readers realized the hours spent in producing a single article which read so easily and so clearly.

It is essential to mention the part that Mrs. Davis played in all of this work. Caroline Davis worked equally hard in these endeavors and the two made a perfect team. She contributed many, many hours to the production of the journal of the Rubber Division. In many respects it was a joint editorship, although her name never appeared in print.

Through his correspondence with the world's figures in rubber chemistry, C. C. Davis developed a wide friendship. In addition to everybody's respect for his technical knowledge, the warmth of his personality was evident in all his correspondence. Although many of the people with whom he had these contacts never saw him face to face, they regarded him as a valued friend.

There were other milestones in his work in the field of rubber literature. After three years of preparation, the American Chemical Society monograph "Chemistry and Technology of Rubber" appeared. It apparently filled an intense need and became the standard reference work in the field of rubber chemistry. There were several reprintings. In the years before 1954, he was associated with G. S. Whitby and R. F. Dunbrook in editing the companion volume "Synthetic Rubber." Although he felt unable to carry the major portion of the work of producing this book, his wide experience was of invaluable help in making it the authority in the field of synthetic rubber.

He contributed a section in Marks' "Mechanical Engineers Handbook" and wrote a chapter in the "History of the American Chemical Society."

In 1950, he and the Division of Rubber Chemistry were honored by the award to him of the Charles Goodyear Gold Medal. This acclaimed his pre-eminence in the field of rubber literature. His lecture on this occasion reflected other facets of his interests. He chose as his title "Some of the Real Pioneers in the Rubber Industry." This allowed him to display his abounding interest in the history of rubber chemistry. Although it dealt necessarily with the technical accomplishments of people who had contributed to the growth of our industry, it was evident that he was also interested in these contributors as people. Their triumphs and vicissitudes through his story made them real and human rather than impersonal workers. His story displayed also the keen and subtle sense of humor of which so many of us were well aware.

I must introduce a personal note. I knew Carroll Davis for over thirty years. We were closely associated in a number of undertakings. Our many contacts were on a wide variety of subjects. Much of this was technical but our friendship covered a lot of territory. Our conversations were always stimulating and constructive. My own personal loss is great.

JOHN T. BLAKE

PREFACE TO *RUBBER REVIEWS*

This is the first issue of *Rubber Reviews*, which is being published as the final issue of Volume XXX (1957) of RUBBER CHEMISTRY AND TECHNOLOGY. It is the hope and wish of the Editorial Board of *Rubber Reviews for 1957* that review issues will appear each year and become an important and valuable addition to the excellent journal that has been published for 30 years by the Division of Rubber Chemistry of the American Chemical Society.

A growing pressure for improving the educational and literature facilities for chemists, engineers, and technologists in rubber and associated industries was becoming very evident, and A. E. Juve, the 1956 Chairman of the Division of Rubber Chemistry, in January 1956 appointed a New-Publications Committee to survey the currently available books dealing with rubber science and technology and to make recommendations to the Division regarding the need for new writings in order to bring the rubber literature up to date. In May 1956 this Committee made a report, which stated in part, as follows:

"Since the preparation of a comprehensive book on the science and technology of rubber would be an enormous task, involving a great many contributors, and since a long time would probably elapse before the last chapters are submitted to the editors, it may be advisable to publish the various chapters of such a book as short monographs as they are completed. In this way the book would be prepared, so to speak, on an installment plan. Those chapters which are completed early would then not have to wait for the late chapters before they are published. Also, any of the chapters could be revised and republished as they become out of date, without waiting for the revision of the whole book. It may be possible to incorporate these monographs into a fifth issue each year of RUBBER CHEMISTRY AND TECHNOLOGY and send them to all members of the Division of Rubber Chemistry. This would reduce the cost of publication and give the monographs a rather wide circulation."

As a result of this report an Editorial Board for *Rubber Reviews for 1957* was appointed by A. E. Juve, and later re-appointed by B. S. Garvey, Chairman of the Division for 1957. The articles in the present issue are the result of the selection by this Board. An Editorial Board for *Rubber Reviews for 1958* has been appointed by R. F. Dunbrook, Chairman of the Division for 1958, and this Board is at present actively engaged in selecting articles for review in the following year.

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INTRODUCTION

The rate of progress of research is such that any comprehensive treatise on rubber ceases to be comprehensive and up-to-date not long after its appearance. The rapidity of the progress that makes this so is owing to several factors but mostly to the great vigor with which today the field of synthetic elastomers and the chemistry and physics of polymers generally are being explored. These areas of knowledge are still in a relatively early stage of development. They extend into vast regions of yet unexplored territory, and only the slightest effort of the imagination is needed to realize that they hold very great possibilities for the development of new products possessed of novel properties and for the achievement of new and deeper insight into elastomeric behavior.

Thanks in considerable measure to progress in the areas of synthetic elastomers and of polymers generally, research on natural rubber also is at a high level of activity, and, within its more limited scope, is marked by a good rate of progress. *Rubber Reviews* is the name of a special issue of RUBBER CHEMISTRY AND TECHNOLOGY. This issue which in each year will be the final one, should be of value in helping those interested in rubber to keep up with all this progress, by presenting reviews of newly-opened aspects and by offering up-to-date accounts of advances in respect of older aspects.

Twenty years have passed since the publication, under the sponsorship of the Division of Rubber Chemistry of the American Chemical Society, of the ACS monograph "The Chemistry and Technology of Rubber", edited by C. C. Davis, and J. T. Blake. The volume of new work on rubber in the years that have succeeded has been so great that the preparation of an exhaustive, up-to-date new treatise, to take the place of the old one, would be a very formidable undertaking and would at best occupy a period of several years. In view of this, the Committee on New Publications appointed by the Division early in 1956 decided to recommend that, in lieu of such a new treatise, the need for something more up-to-date than "Davis and Blake" could perhaps best be met by publishing, gradually, in RUBBER CHEMISTRY AND TECHNOLOGY, articles in which the present state of knowledge of the major divisions of the subject of rubber would be set forth. Such articles, it was contemplated, would in effect represent what might have been individual chapters of a new Davis and Blake, and, as such successive reviews appeared, all the more important aspects of rubber chemistry and technology would be kept covered by up-to-date surveys. Accordingly, after much study, it was decided to publish annually a special issue of RUBBER CHEMISTRY AND TECHNOLOGY to be known as *Rubber Reviews*. This issue though not a new journal, has some of the aspects of one. The cover will have a distinctive color and will bear the name in prominent type. Many members of the division may wish to bind this issue separately.

In many of the applications of rubber, including tires, the property or the complex of properties involved in the possession of a high degree of resilience along with a low dynamic modulus is of more dominating importance than ultimate strength and extensibility at rupture. And because of a growing

realization of this, much study has been given in recent years to the dynamic behavior of rubber under rapid, small deformations. The fact that in the behavior of organic elastic materials of low dynamic modulus there is a viscous as well as an elastic aspect, makes the subject one of considerable complexity. A welcome review of this subject—of its theory, of the experimental devices developed for its study, and of some of the factors concerning the molecular structure and compounding of natural rubber and of synthetic elastomers that influence dynamic properties—is presented in the leading article entitled "Dynamic Properties of Elastomers". It may be hoped that before long the studies there reviewed will lead to the development of standardized testing methods the adoption of which will contribute substantially to the evaluation of new elastomers and to improvements in the compounding of rubber destined for use under dynamic conditions.

An examination of the chapter "Theories and Phenomena of Vulcanization" in Davis and Blake makes it apparent that twenty years ago very little progress had been made toward an understanding of the reaction, vulcanization, on which rubber manufacturing uniquely depends. Since then, thanks in part to the investigation of the action of sulfur (with and without other curing ingredients) on simple, model molecules, substantial progress has been made toward an understanding of the chemistry of vulcanization, although it would be wrong to claim that all aspects of the subject have yet been elucidated. A review of the new results relative to the mechanism of the chemical reactions involved in vulcanization and relative to the nature of the crosslinks formed thereby and an interpretation of these results is offered in the article herein "The Vulcanization of Rubber with Sulfur".

Another subject on which considerable progress has been made in recent years—here again in a measure as a result of studies on simple, model molecules—is the autooxidation of the unsaturated polymer molecules of which rubber and other elastomers are composed. A review of the current state of knowledge on this subject is given in the article "Aging and Oxidation of Elastomers."

With the incoming of synthetic rubber as a major raw material of rubber-goods manufacturing, carbon black has assumed an importance in rubber compounding even greater than it possessed before the war. Synthetic-rubber goods are in general dependent for their strength on compounding with black even more than natural-rubber goods are. And since synthetic rubber came into use on a large scale, the whole subject of carbon black has become more intricate than it was before the war. Many new types and grades of black have been introduced, and a large volume of new research work has been done on the physics and chemistry of blacks and their influence on the behavior of rubber. In the article on Carbon Black in the present issue of *Rubber Reviews*, the emphasis is on the *chemistry* of the subject. The article, though frankly acknowledging that much remains obscure in this matter, reviews what is now known about the chemically-reactive groups on carbon black particles and the ways in which such groups may influence vulcanization and reinforcement.

In addition to major articles designed to offer full accounts of the present state of knowledge in the main divisions of rubber chemistry, physics, and technology, *Rubber Reviews* will include articles on recent developments of narrower range—developments of immediate and topical interest. Examples of such developments are covered by the article on "Carboxylic Rubbers" and that on "Basic Elastomers" included in the present issue. Both these articles illustrate the ready possibilities of making synthetic elastomers possessed of novel properties by the inclusion in the monomer mixture of a rela-

tively small proportion of a special component containing a chemically reactive grouping. In the carboxylic rubbers this component is a polymerizable carboxylic acid, which, by introducing carboxyl groups into the elastomer, renders the rubber readily susceptible to a wide variety of crosslinking reactions. A tensile strength as high as 11,000 psi is reported as having been secured in a gum stock of a nitrile copolymer comprising a carboxylic component, merely by heating the material with twice the amount of zinc oxide needed to react with the carboxyl groups present. In the basic elastomers the special component is a vinylpyridine or a homolog of such, which, when the copolymer is compounded with suitable organic halogen compounds (e.g., benzal chloride), forms quaternary addition products that possess notable resistance to oils.

The highly polar groups present in the carboxylic rubbers and in the basic elastomers affect the wetting power of the polymers, and this is reflected in the possession of interesting adhesive properties and in their surface relationship of the polymers to inorganic fillers, which produce stiffer stocks with them than with corresponding elastomers in which polar groups are lacking.

Plans for subsequent issues of *Rubber Reviews* are not complete, but it may be mentioned that among the subjects it is hoped to cover in early issues are reviews dealing with both old and new aspects of rubber science and technology. Those now in various stages of completion are: "The Analysis of Elastomers", "The Crystallization of Elastomers", and "The Kinetic Theory of Elasticity". Natural rubber latex and the physical aspects of reinforcement will receive early attention in *Rubber Reviews*.

G. Stafford Whitby

DYNAMIC PROPERTIES OF ELASTOMERS

S. D. GEHMAN

RESEARCH DIVISION, THE GOODYEAR TIRE AND RUBBER CO., AKRON, OHIO

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I. INTRODUCTION

The large volume uses of rubber involve its cushioning, quieting, vibration-energy absorbing and isolating characteristics. Applications such as tires, belts, and engine mounts employ rubber under conditions of rapidly repeated deformations which are relatively small compared to ultimate breaking values. Although ultimate values and fatigue tests are important as criteria of quality, they are of no assistance to the engineer, designer or technologist for anticipating the response of his product to the forces experienced in service. To fill this need, there has grown up a body of technical and scientific methods, data, and principles usually referred to as the field of dynamic properties.

The term dynamic properties as applied to elastomers usually means vibration properties which are displayed in response to sinusoidal forces. But restriction to sinusoidal forces is unduly narrow. In principle, both theory and experiment can be extended to more complex force patterns, such as square or saw tooth waves, if there is occasion to do so. The distinctive feature of the field of dynamic properties lies, perhaps, more in the amplitudes of the deformations, which are relatively small, than in the force diagram or the frequency. Results at quite low frequencies are sometimes included in work regarded to be on dynamic properties but the amplitudes are always rather small. In polymer science, the field of dynamic properties has tended to be restricted to amplitudes so low that the properties are essentially linear. This would provide a convenient definition but it is an unacceptable limitation from a technological standpoint where it is highly desirable to extend the work into the nonlinear region. On the other hand, fatigue and failure phenomena are definitely excluded from consideration here. Ordinary tensile stress-strain tests have a dynamic aspect but such results are not included in the catagory of dynamic properties. The field to be known as the dynamic properties of elastomers logically comprises the properties exhibited in response to periodic or transient forces for all types of deformation small enough not to induce appreciable fatigue or failure during the investigation. There is no good reason for limiting the frequency on either the low or high side. Temperature is, of course, a most important variable.

Dynamic properties assumed increasing technological significance for the development of synthetic rubbers. Examination with dynamic test procedures as compared to the conventional tests gave judgments of the essential rubberlike character of the elastomers, their ability to respond to rapid deformations of low amplitude in a rubberlike way. Furthermore, the results provided an evaluation of energy losses and relative heat generation which turned out to be properties of paramount importance for the use of synthetic

rubber in tires. This development was covered in a previous review[1]. There has occurred, largely since then, a notable enlargement of the phenomenological theory of the dynamic behavior of polymers[2]. This fits dynamic behavior into the general framework of the response of viscoelastic materials to all types of forces. Although the theory has serious limitations for technological purposes, it does provide a background and understanding which, in some cases, can increase tremendously the significance and scope of limited dynamic results. A brief and elementary account of a few of the most useful aspects of these general considerations follows.

II. DYNAMIC PROPERTIES AND THE THEORY OF VISCOELASTICITY

Illustrative analysis for a model.—The simpler concepts of the theory are illustrated with the aid of mechanical models. These models, consisting of

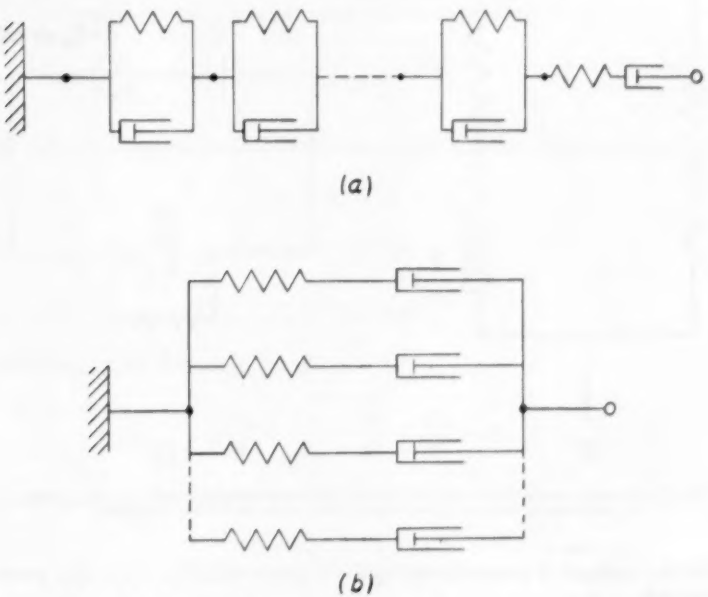


FIG. 1.—Equivalent "canonical" forms of mechanical models which show viscoelastic behavior. Model (a) consists of Voigt elements in series and Model (b) of Maxwell elements in parallel.

springs and dashpots connected in diverse ways, can simulate various aspects of the mechanical behavior of elastomers. A comprehensive model to account for a variety of viscoelastic phenomena may become quite complex with spring and dashpot units inserted in special ways to explain each aspect of viscoelastic behavior such as creep, stress relaxation, set, etc. However, Roscoe[3] showed that all such models can be reduced to either of the two canonical forms illustrated in Figure 1 and formulated rules for transposing from one type to the other. Use of one or the other of these forms generally leads to economy in

the number of springs and dashpots required. The two forms are mathematically equivalent and, in fact, are also equivalent to using a differential equation to express the relationship between stress, strain, and time.

The analysis for a relatively simple model will help in understanding dynamic properties and in visualizing how they are related to other viscoelastic phenomena such as creep and stress relaxation. A suitable model for these purposes is shown in Figure 2. This model is described as consisting of a Maxwell unit, i.e., a spring and dashpot in series, in parallel with a spring. All of the components of the model are linear in the sense that the stretch of either spring is proportional to the force which stretches it and the frictional

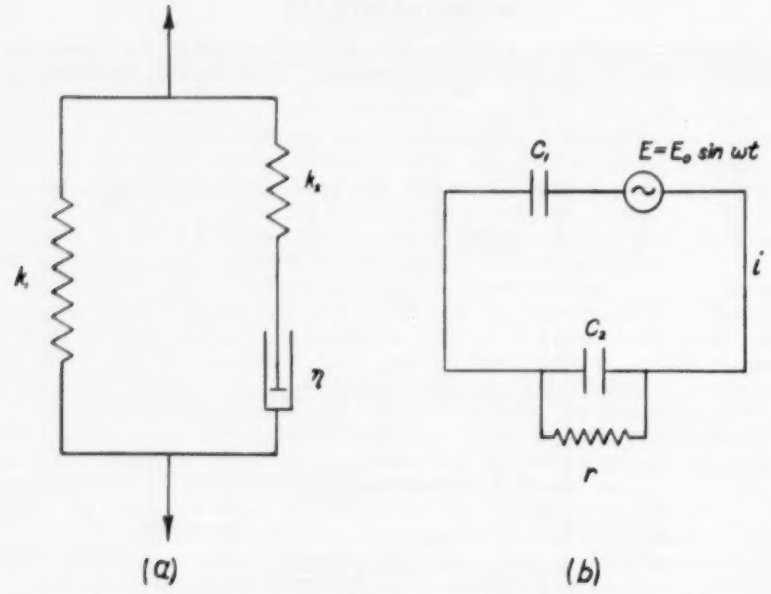


FIG. 2.—A simple mechanical model and its electrical circuit analog suitable for illustrating the relationship between dynamic properties, creep, and stress relaxation.

force in the dashpot is proportional to the relative velocity of the two parts of the dashpot.

The general solution to the problem would be to formulate the response or deformation of the model for any arbitrary force-time function. But experiments to determine viscoelastic properties are usually carried out by making one or more of three relatively simple series of measurements, viz., stress relaxation at constant length; creep under constant load; dynamic modulus and internal frictional losses with an applied sinusoidal force. In theory, the same information can be obtained from any of these procedures but there are practical considerations which usually lead to the choice of a particular method depending upon the purpose of the experiment. Assistance can be obtained in visualizing the general relations between the results from these three experimental procedures by considering the solutions for the model.

SOLUTIONS FOR SPECIAL CASES

1. *Stress relaxation at constant stretch.*—If f_1 is the force applied to the spring which has stiffness k_1 and the extension of the spring is x_1, then

$$f_1 = k_1 x_1 \tag{1}$$

Similarly

$$f_2 = k_2 x_2 \tag{2}$$

The extension of the dashpot, x_3, will obey the equation

$$f_2 = \eta \frac{dx_3}{dt} \tag{3}$$

η is the "viscosity" of the dashpot defined by Equation 3 as the constant of proportionality between the velocity and the force.

The relaxation time of the Maxwell unit is defined as

$$\tau = \frac{\eta}{k_2}$$

If x_0 is the constant stretch of the model and f is the stretching force,

$$x_0 = x_1 = x_2 + x_3 \tag{4}$$

$$f = f_1 + f_2 = k_1 x_1 + k_2 x_2 \tag{5}$$

$$f_2 = k_2 x_2 = \eta \frac{dx_3}{dt} \tag{6}$$

Differentiating Equation (4) gives

$$\frac{dx_0}{dt} = \frac{dx_1}{d'} = \frac{dx_2}{dt} + \frac{dx_3}{dt} = 0 \tag{7}$$

So that Equation (6) may be written as

$$\frac{k_2}{\eta} = -\frac{1}{x_2}\frac{dx_2}{dt} \tag{8}$$

Solution of Equation (8) for x_2 and substitution in Equation (5) gives

$$f = x_0(k_1 + k_2 e^{-k_2 t/\eta}) \tag{9}$$

Since $x_2 = x_0$ at $t = 0$.

2. *Creep under constant load.*—Let f_0 be the constant stretching force. Then by adaptation to this condition of the same type of reasoning as above, it follows that

$$x = f_0\left(\frac{1}{k_1} - \frac{k_2}{k_1(k_1 + k_2)}\, e^{-t/\tau}\right) \tag{10}$$

where

$$\tau = \eta\left(\frac{1}{k_1} + \frac{1}{k_2}\right)$$

It is apparent that either measurements of f as a function of t (Case 1) or of x as a function of t (Case 2) will provide sufficient information to determine all the constants for the model and thus to specify it completely so that the response to any force function could be calculated.

3. *Sinusoidal applied force.*—The deformation of the model for a sinusoidal force, $f = f_0 \sin \omega t$, corresponding to dynamic testing, can be obtained in several ways. For instance, it follows from appropriate integration of the fundamental equations derived from the Superposition Principle for viscoelastic behavior[2]. Or, the differential equation of motion for the model can be written down and solved. A powerful, general method for securing the steady state response of such models to a sinusoidal force is to make use of an analogy to electrical networks. Graphical methods for solving electrical networks could then be used. Or, preferably, the highly developed operational methods for electrical circuits and the properties of impedance functions can be applied. In the electrical analogy[2], electromotive force corresponds to stress, current to the rate of change of strain, capacitance to the reciprocal of spring constant and resistance to dashpot viscosity. Elements, i.e., springs and dashpots, which are in parallel in the mechanical model must be coupled in series in the electrical network and vice versa.

The electrical network corresponding to the mechanical model in Figure 2(a) is shown in Figure 2(b). The impedance of this circuit, the complex ratio of EMF to current, can be written down directly from elementary rules for alternating current networks as:

$$Z = \frac{E}{i} = \frac{1}{jC_1\omega} + \frac{1}{\frac{1}{r} + jC_2\omega} = \frac{1}{jC_1\omega} + \frac{r}{1 + jrC_2\omega} \tag{11}$$

where i is the current in the network. Separation of this expression into its real and imaginary parts gives Z in the form

$$Z = R + jX \tag{12}$$

The current is

$$i = \frac{E_0}{|Z|} \sin(\omega t - \alpha) \tag{13}$$

or

$$i = \frac{E_0}{|Z|} (\sin \omega t \cos \alpha - \cos \omega t \sin \alpha) \tag{14}$$

where

$$|Z| = \sqrt{R^2 + X^2} \tag{15}$$

and

$$\tan \alpha = \frac{X}{R} \tag{16}$$

The value for $|Z|$ obtained from Equations (11), (12), and (15) is

$$|Z| = \frac{1}{C_1\omega} \sqrt{\frac{1 + r^2\omega^2(C_1 + C_2)^2}{C_2^2 r^2 \omega^2 + 1}} \tag{17}$$

To go from the electrical analogue to the mechanical model, there are the following relations:

$$C_1 \rightarrow \frac{1}{k_1} = \mu_1; \quad C_2 \rightarrow \frac{1}{k_2} = \mu_2; \quad r \rightarrow \eta$$

$$E_0 \rightarrow f_0; \quad i \rightarrow \frac{dx}{dt}$$

If $|Z|$ is now the mechanical impedance, these relations and Equation (17) give

$$|Z| = \frac{1}{\mu_1 \omega} \sqrt{\frac{1 + \eta^2 \omega^2 (\mu_1 + \mu_2)^2}{\mu_2^2 \eta^2 \omega^2 + 1}} \tag{18}$$

$$\frac{dx}{dt} = \frac{f_0}{|Z|} \sin(\omega t - \alpha) \tag{19}$$

$$x = -\frac{f_0}{|Z|\omega} \cos(\omega t - \alpha) \tag{20}$$

$$x = -\frac{f_0}{|Z|^2 \omega} (X \sin \omega t + R \cos \omega t) \tag{21}$$

Where X and R are now the mechanical equivalents of the electrical quantities defined by Equations (12) and (14). The phase angle between the force and deformation is

$$\delta = \alpha + \frac{\pi}{2} = -\tan^{-1} \frac{R}{X} \tag{22}$$

Setting

$$\tau = \eta(\mu_1 + \mu_2); \quad \beta = \frac{\mu_1}{\mu_2}$$

and substituting the values of $|Z|$, R, and X in Equation (21) gives

$$x = \frac{f_0}{k_1 + k_2} \left\{ \sin \omega t + \frac{\beta}{1 + \omega^2 \tau^2} \sin \omega t - \frac{\beta \omega \tau}{1 + \omega^2 \tau^2} \cos \omega t \right\} \tag{23}$$

The form of the solution illustrates the general character of the response of a viscoelastic material to a sinusoidal driving force. The first term is a component of the displacement which is in phase with the alternating force and represents the instantaneous or ordinary elastic response which is independent of frequency. The second term is also in phase with the force but is frequency dependent. It represents the elastic component of the viscoelastic response. The third term is frequency dependent, is 90° out of phase with the force and is responsible for the energy losses. It has its maximum value when $\omega = 1/\tau$. Thus experimental observation of such a maximum for a material permits an order of magnitude estimate of the mean relaxation time for the material. The maximum occurs when the vibration period approximates the mean relaxation time. The resultant displacement from the three terms in Equation (23) will have a phase difference with the force which will depend upon the

ratio of the in-phase and out-of-phase components. This situation is usually represented by considering the dynamic shear modulus to be a complex quantity

$$G^* = G' + iG'' \tag{24}$$

The operator i is the mathematical tool which takes account of the 90° phase difference between G' and G''. G' is the component of stress in phase with the strain divided by the strain and is called the real component of the dynamic modulus or the storage modulus. G'' is the component of stress which is 90° out of phase with the strain, divided by the strain and is the imaginary component of the dynamic modulus or the loss modulus. The ratio G''/G', is the tangent of the phase angle δ by which the stress leads the strain and is called the loss tangent.

From Equation (23), it can be seen that at high frequencies, where $\omega\tau \gg 1$, the deformation is

$$x = \frac{f_0}{k_1 + k_2} \sin \omega t \tag{25}$$

At high frequencies, the dashpot is essentially rigid, the energy loss per cycle approaches zero and the displacement is in phase with the force. For a gum rubber vulcanizate at room temperature, a frequency of the order of several megacycles per second is required to show these effects. At lower temperatures, audio frequencies are adequate.

At low frequencies, $\omega\tau \ll 1$, the velocity of the dashpot is so small that the energy losses are negligible, the spring in series with it does not participate in the displacement and the deformation is simply:

$$x = \frac{f_0}{k_1} \sin \omega t \tag{26}$$

These limiting cases serve to illustrate that, except at frequencies very large or very small compared to τ, the apparent stiffness and hence the amplitude of deformation for a given driving force depends on the frequency. The amplitude decreases monotonically as the frequency is increased. The loss tangent, however, goes through a maximum value at some intermediate frequency since it is zero for both very high and very low frequencies. From Equations (16), (21), and (23),

$$\tan \delta = \frac{\beta\omega\tau}{1 + \beta + \omega^2\tau^2} \tag{27}$$

$\tan \delta$ has its maximum value when

$$\omega\tau = \sqrt{1 + \beta} = \sqrt{\frac{k_1 + k_2}{k_1}}$$

If the "instantaneous" or ordinary elastic component is negligible, $\tan \delta = \omega\tau$.

Figure 3 illustrates how the amplitude and losses depend upon the frequency. The highest energy losses occur where the period is comparable to τ. Here also the amplitude changes most rapidly with frequency. This is called the

dispersion region. With actual viscoelastic materials the dispersion region, i.e., the region where the dynamic properties depend on the frequency, is usually very broad and extends over many decades of frequency.

Distribution function of relaxation times.—The analysis of the dynamic response of this very simple model serves the purpose of illustrating the pattern of the results to be expected when relaxation mechanisms are present. In this case, there was only one relaxation time, but obviously many elements might be included in such a model with a large range of relaxation times. Since the dynamic response of viscoelastic materials exhibits, in a general way, the same sort of pattern, viscoelastic theory associates the relaxation times with molecular mechanisms such as the coiling and uncoiling of polymer molecules or the coordinated motions of segments of the molecules. Obviously, a large range of

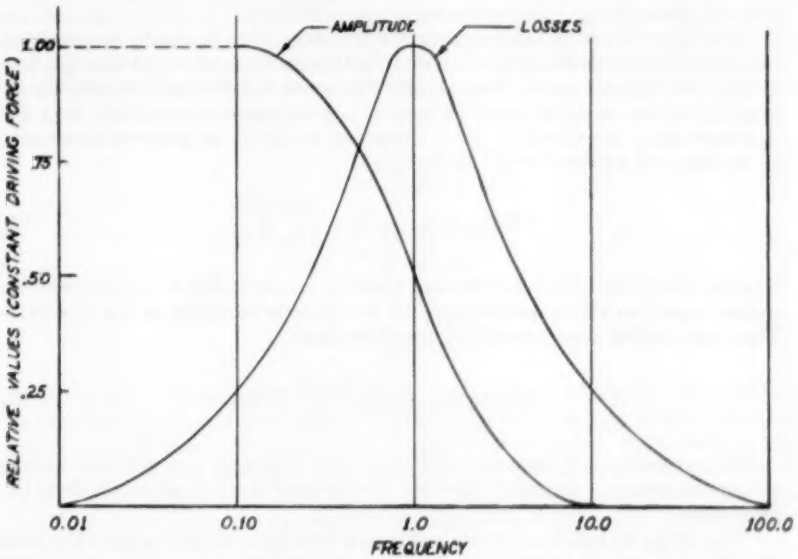


FIG. 3.—Dependence of amplitude and losses on the frequency for a viscoelastic material with one relaxation time. The maximum energy loss occurs when the period of the driving force coincides with the relaxation time. For actual materials, the position of the peak gives an indication of the average relaxation time.

relaxation times will be involved, the longer times being connected with motions of larger units of structure. To account for viscoelastic phenomena observed for polymers, it has been advantageous to work with the concept of a continuous distribution of relaxation times[3,4]. Just as in the case of a model with discrete relaxation times, any experimental procedures such as creep or stress relaxation measurements which are adequate to discover the distribution of relaxation times for a material will, in theory, enable the prediction of the dynamic properties. The distribution function of relaxation times is actually a weighting function which specifies the contribution to any type of viscoelastic response of relaxation times lying in the interval between τ and $\tau + d\tau$. Usually a logarithmic scale is used for τ and the definition changed so that the function defines the contribution at τ for relaxation times in the range $d(\log \tau)$.

The following equations are formulations for the dynamic properties in terms of the distribution of relaxation times[4], $H(\log \tau)$.

$$G'(\omega) = \int_{-\infty}^{+\infty} H(\log \tau) \left[\frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} \right] d \log \tau \tag{28}$$

$$G''(\omega) = \int_{-\infty}^{+\infty} H(\log \tau) \left[\frac{\omega \tau}{1 + \omega^2 \tau^2} \right] d \log \tau \tag{29}$$

$$\eta' = \int_{-\infty}^{+\infty} H(\log \tau) \left[\frac{\tau}{1 + \omega^2 \tau^2} \right] d \log \tau \tag{30}$$

η' is the dynamic viscosity or internal friction.

If G' and G'' are known as analytical functions of ω, it should be possible to determine $H(\log \tau)$, the relaxation distribution function or relaxation spectrum as it is sometimes called. But usually this is not feasible mathematically and approximation methods must be used[2,4]. It has been shown that to a first approximation the function can be obtained by point to point measurements of the slope of a plot of $G'(\omega)$ vs $\log 1/\omega$

$$[H(\log \tau)]_{\tau=1/\omega} \cong - \frac{d\, G'(\omega)}{d \log 1/\omega} \tag{31}$$

That is, the value of the distribution function at any point $\tau = 1/\omega$ is approximately equal to the negative slope of the storage modulus vs $\log 1/\omega$ curve. The same sort of approximation procedure gives

$$[H(\log \tau)]_{\tau=1/\omega} \cong \frac{4.606}{\pi} G''(\omega) \tag{32}$$

By comparison of Equations (31) and (32), it is seen how the loss modulus at any frequency is related to the rate of change of the storage modulus at that frequency.

The $H(\log \tau)$ function is obtainable to a first approximation from the negative slope of a shear stress relaxation curve in which the relative stress is plotted against $\log t$.

$$[H(\log \tau)]_{\tau=t} \cong - \frac{1}{S_0} \frac{d\, S(t)}{d \log t} \tag{33}$$

Here S_0 is the initial stress and $S(t)$ that at a subsequent time t. Comparison of Equations (32) and (33) relates the loss modulus to the negative slope of the stress relaxation curve.

The same type of information can also be obtained from suitable creep curves. Thus in theory, results from any of these experimental procedures are adequate to describe completely the viscoelastic behavior of a material, including the dynamic properties. As a practical point, creep and stress relaxation procedures are best suited for securing information on the longer relaxation times and dynamic tests for the shorter times. Hence the methods may very well supplement rather than substitute for each other. Furthermore, stress relaxation and creep measurements are frequently used to study

chain scission and other chemical changes the occurrence of which, of course, would vitiate any of the comparisons under consideration here. Both the static and dynamic results follow from the character of the distribution of relaxation times for the material so that this distribution furnishes the basis for correlations of static and dynamic measurements. In principle, the theory teaches that in comparing materials over a range of the variables of frequency, temperature, or time, the energy losses will be relatively smaller if and where the storage modulus, relaxing stress, or creep are changing more slowly.

Nomenclature.—For many purposes, it is more convenient to express the dynamic response of a viscoelastic material in terms of a complex compliance J^* with components J' and J'' rather than in terms of a complex modulus. In defining J' and J'', the strain is resolved into two components, one in phase with the stress and the other lagging 90°. This is in contrast to the procedure for defining G' and G'' in which case the stress was resolved into two components, one in phase with the strain and the other leading by 90°. The storage compliance, J', is the ratio of the amplitude of the component of the strain in phase with the stress to the stress and the loss compliance J'' is the corresponding ratio for the out-of-phase component.

$$J'^2 + J''^2 = \frac{1}{G'^2 + G''^2} \tag{34}$$

$$J' = \frac{G'}{G'^2 + G''^2} \tag{35}$$

$$J'' = \frac{G''}{G'^2 + G''^2} \tag{36}$$

An effort is being made to establish a consistent, comprehensive nomenclature for viscoelastic quantities[5]. In this system the letters G and J as used above refer to shear stressing. For longitudinal stressing, the corresponding use of E and D is proposed. The distribution or spectrum of relaxation times as presented in Equations (28) to (30) for completeness is supplemented by a distribution or spectrum of retardation times which apply for creep and the dynamic compliances.

Equivalence of frequency and temperature variations.—The study of families of creep curves for polymeric materials observed for a range of temperatures led to the observation that the effect of raising the temperature was merely to contract the time scale[2]. Change in temperature had the effect of displacing a creep curve along the log time axis. This is an example of what has become known as the time-temperature superposition principle[6]. It is one of the most useful and illuminating contributions from the theory of viscoelasticity. Decreasing the temperature has effects similar to increasing the frequency and vice versa.

The range of frequencies available with any one apparatus for measuring dynamic properties is usually rather limited. This is especially the case with simpler equipment suited for technological testing and development purposes. By making the measurements over a range of temperatures, the frequency capabilities can, in effect, be extended enormously. The principle has been tested over ranges as great as twenty decades of frequency and time[6,7]. A complete diagram of the frequency dependence such as that shown in Figure 3

is rarely obtained because of the tremendous frequency range required to elicit such behavior from elastomers. However the phenomena illustrated by the curves are very familiar when temperature rather than frequency is the variable[8]. An inverse relationship between frequency and temperature in their effects on dynamic properties is indicated indirectly by the solution for the mechanical model given by Equation (23). For a material corresponding to such a model, it would be expected that the effect of temperature would be predominantly exerted through its effect on the relaxation time. But the relaxation time appears only in the product $\omega\tau$ so that any change in the response produced by a change in τ could be either simulated or offset by a suitable change in ω.

There are empirical factors involved in interchanging frequency and temperature for a given material but the procedures are relatively simple and have been described and illustrated in detail by Ferry, Fitzgerald, Grandine, and Williams[4]. It is assumed that when the temperature is changed from a reference temperature T_0 to another temperature T, every relaxation time is multiplied by an empirical factor a_T. Reduced variables G'_p, G''_p, and ω_p can then be defined as follows:

$$G'_p = G' \frac{T_0\rho_0}{T\rho} \tag{37}$$

$$G''_p = G'' \frac{T_0\rho_0}{T\rho} \tag{38}$$

$$\eta'_p = \frac{\eta'}{a_T} \frac{T_0\rho_0}{T\rho} \tag{39}$$

$$\omega_p = \omega a_T \tag{40}$$

ρ_0 and ρ are the densities at T_0 and T, respectively. If G'_p and G''_p are plotted against ω_p, a single master curve should be obtained from data for all temperatures and frequencies. The a_T factors can be secured by plotting $\log \eta'(T_0\rho_0/T\rho)$ against $\log \omega$ and shifting the curves into coincidence along a line with slope of -1. The distance moved either horizontally or vertically is $\log a_T$. It is often advantageous to plot the $\log a_T$ values against $10^3/T$. The same a_T factors should be valid for all the linear viscoelastic phenomena observed with a given amorphous polymer.

Williams, Landel, and Ferry[9] have shown a further generalization in regard to the a_T factors for both viscoelastic and dielectric phenomena. If the reference temperature for each polymer is suitably related to the glass transition temperature, T_g, for the polymer, the shift factors should be about the same for all amorphous polymers for temperatures not too far removed from T_g. The reference temperature suggested was $T_s = T_g + (50 \pm 5)°$. The range of applicability is from T_g to about $T_g + 100$. A simplified rougher approximation using T_g rather than T_s was also found and is given below.

$$\log a_T = \frac{-17.44(T - T_g)}{(51.6 + T - T_g)} \tag{41}$$

It is to be noted that the equivalence principle has been extended to apply to the concentration of polymer solutions as well as to time and temperature,

i.e., raising the concentration has effects similar to decreasing the temperature and increasing the frequency.

Investigations of the dynamic properties of vulcanized Buna N compounds by Hutton and Nolle[8] over a frequency range from 0.05 to 20,000 cps and a temperature range from about −20° to 50° C using serveral experimental methods led them to the conclusion that the method of reduced variables was not applicable for vulcanized Buna N rubber over a wide range of temperature and frequency. Thus for temperatures near 25° C and frequencies in the range of 100 to 1000 cps, the effect of a tenfold change in frequency could be compensated for by a temperature change of about 12° C. But for temperatures just above 0° C and frequencies from 0.05 to 1.0 cps a decade of frequency corresponded to only about 3° C change in temperature. There is the possibility on theoretical grounds of a general breakdown in the methods of reduced variables for crosslinked structures at very low frequencies. Hutton and Nolle considered that their results went further than this and showed a phenomenon which had no special relation to crosslinking but rather that mechanisms which govern the temperature dependence of the modulus at low frequencies may not be those viscoelastic mechanisms important for the higher frequencies used. Later Payne[10] showed that the low frequency data, for 0.05, 0.1, and 1 cps could be reduced by using a modified method worked out by Ferry, Grandine, and Fitzgerald[11] in an investigation of the relaxation distribution function for polyisobutylene in the transition region from rubberlike to glasslike behavior. By this procedure, the real and imaginary parts of the complex compliance in a plot against log (ωa_T) were reduced to single curves for all the data. A subtractive correction was made for the glassy compliance, J_g, in reducing the real component. This implies that all contributions to compliance except J_g are inversely proportional to temperature and density and are associated with retardation times all of which have the same temperature dependence. The basic questions raised by Hutton and Nolle in contrasting the effect of temperature on the low and high frequency results with vulcanized Buna N still remain. To reach more definite conclusions on the possible limitations of the method of reduced variables similar investigations may be required on a variety of elastomers. Perhaps in the case of Buna N these difficulties are especially prominent because of large polar molecular forces.

Contributions and limitations of the theory of viscoelasticity.—The major contribution of the theory is, no doubt, the insight and understanding which it provides for the relations between diverse viscoelastic phenomena observed with widely different materials over a large range of variables such as temperature, frequency, and time. It is a descriptive theory and in seeking to apply it to a given elastomer there must always be a core of experimental observations. If the data are adequate, application of the theory should then permit prediction of the viscoelastic behavior for other temperatures, frequencies, and types of force application. Progress is still being made in the development of the theory to reduce the amount of data required for its application. In many cases, mathematical difficulties will permit only approximations from the theory. The mathematical procedures tend to be too involved for routine use in technological evaluations and frequently an impractical amount of data is required to apply the theory fruitfully. The recognition from the theory of various patterns of dynamic behavior and ranges of the variables in which they are exhibited can be very useful. Dynamic properties are brought into the framework of all viscoelastic phenomena. The dynamic modulus is recognized to be a function of frequency and the static modulus a function of time. One

of the most severe limitations of the theory is its restriction to the linear region of response. This requirement has presumably been met with the dynamic measurements used to develop the theory by working with extremely small amplitudes. But usually no information is given as to the upper limit for the amplitude and how this may depend on the frequency, temperature or type of elastomer. Similarly, application of the theory for any other viscoelastic phenomenon such as creep, is limited to deformations sufficiently small that structural changes such as those caused by molecular orientation or crystallization do not occur. Such small deformations usually put measurements of technological interest outside of the limits of strict applicability of the theory. The theory is especially adapted for securing a comprehensive picture of the viscoelastic behavior of a material over a wide range of the variables, frequency temperature, and time. Technological interest, however, often resides in knowing how the behavior changes over a relatively small range of these variables but for systematic changes in composition, structure, and molecular parameters such as crosslinking and molecular weight distribution. The theory is of little help in such endeavors. There are usually only one or two dispersion regions and these, as a rule, are too broad to resolve any details due to molecular structure. Some exceptions to this will be noted later.

Mention should be made of doubts and misgivings which have been expressed in regard to the mathematical logic used in the interpretation of the results of dynamic experiments under forced sinusoidal vibrations[12]. The concept of an elastic constant and viscosity which are dependent on frequency has been challenged as highly illogical and merely a reflection of a more fundamental dependence of the stress upon higher time derivatives of the strain. These "constants" can be expressed in terms of frequency only because the problem has a sinusoidal solution and this case may disguise a possibly highly nonlinear fundamental equation. Although some of the general, mathematical implications of expressing the stress in terms of higher time derivatives of the strain have been explored, this more sophisticated approach has not been developed to the point where it can contribute as much to the interpretation and use of the experimental data as the conventional, albeit illogical, concepts now in use.

III. METHODS OF MEASURING DYNAMIC PROPERTIES

Already in 1940, Mooney and Gerke[13] observed that "the mechanical hysteresis of rubber has been measured by almost every conceivable method". But ever since then procedures for determining dynamic properties and hysteresis losses have continued to multiply with apparently limitless ingenuity and imagination, testifying to the fascination of this type of experimentation and perhaps also to the quest for the elusive, ideal method. Actually, many of the more recent procedures are variations and improvements based on older principles. Often the methods should yield fundamentally the same type of information although the results may be differently expressed. Several comparisons of methods of making dynamic measurements have appeared[1,4,14]. The discussion which will be given here provides a few illustrative examples of significant work in recent years with the various methods, the emphasis being on investigations of technological interest. No attempt will be made to generalize on the precision, virtues, and shortcomings of the methods because these characteristics of the experimenter are also inextricably involved in the overall results. The accomplishments with a given method depend very much on the state of development in which it is found and the skill of the investigator.

The following classification is followed.

A. Free vibration methods
B. Forced vibration methods
   1. Nonresonance
   2. Resonance
C. Propagation methods
   1. Continuous waves
   2. Pulses

Free vibration methods.—The freely oscillating torsion pendulum is a classical instrument in rubber research and technology. It has taken many forms. The amplitude of the initial oscillation decays with successive swings and this decay provides a measure of the energy loss. The frequency of oscillation gives information for calculating the dynamic modulus. There is always a dependence of the frequency on the particular sample used and usually a limitation to two or three decades of frequency, achieved by varying the oscillating mass, the sample size and shape or by the use of an auxiliary stiff torsion wire[15]. Periods are usually of the order of 0.02 to 30 sec. Since the apparatus is compact at the sample, temperature control is relatively convenient and the effective frequency range can be very large if the principle of the equivalence of temperature and frequency changes is established and used for the materials being investigated. The character of the stresses in the testpiece may require consideration. Ecker[16] used a tubular test specimen to minimize the radial variation of shearing stress which always exists. Gent[16] has given an analysis of effects of the shape of torsional test specimens. Small initial elongations which may be uncontrolled unless special measures are taken cause a remarkable reduction in the internal friction. Ten per cent extension of a rubber gum compound caused a decrease of about 25 per cent in the dynamic viscosity[17]. Kuhn and Künzle[17] suggested that extension of tangled chain molecules in the longitudinal direction favored gliding in planes parallel to this direction and thus reduced the dynamic viscosity. Another complication is that for large extensions the stretching force has the effect of producing an additional torque around the vertical axis. To better control the stresses in the test specimen, the weight of the oscillating mass can be supported by a long thin wire[17]. Nielsen[15] used an extrapolation procedure to secure results corresponding to zero stretching force.

The oscillations have usually been measured by means of a pointer rotating over a protractor, a light beam and scale, or a light beam the trace of which is recorded photographically. A more recent development is to use electronic instrumentation, picking up the oscillations with a sensitive transducer such as a linear differential transformer, amplifying the output with appropriate circuitry and feeding it into a chart recorder[18], see Figures 4(a) and 4(b).

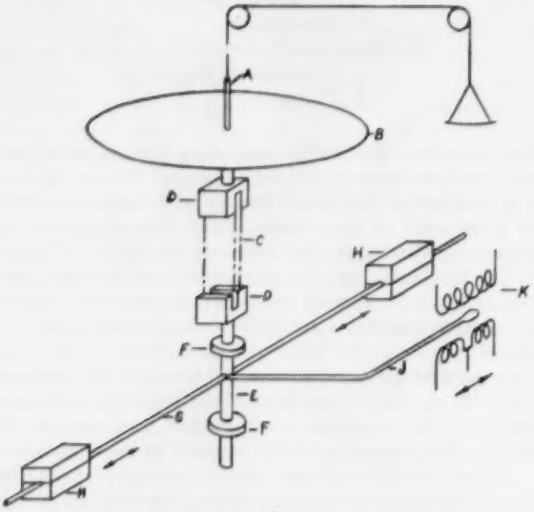
The decay of the amplitude, illustrated in Figure 5, is related to the energy losses, already discussed for forced vibrations, in the following way if the damping is small

$$\frac{G''}{G'} = \frac{4\pi\lambda}{4\pi^2 + \lambda^2} \tag{42}$$

$$\lambda \cong \pi \frac{G''}{G'} \cong \frac{\pi\eta p_a}{G'} \cong \pi \tan\delta \tag{43}$$

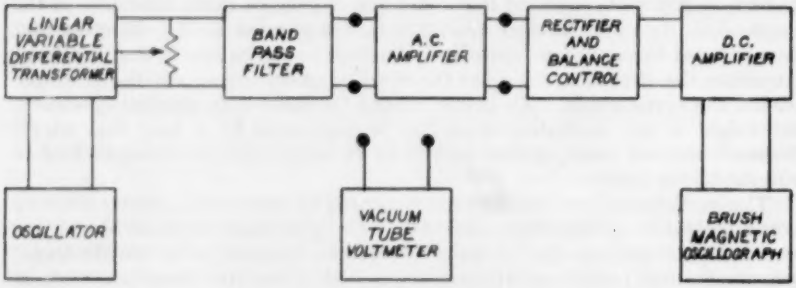
λ is the logarithmic decrement, i.e., if A_1 and A_2 are the amplitudes for two successive oscillations,

$$\lambda = \log_e \frac{A_1}{A_2} \tag{44}$$



(a)

FIG. 4(a).—Schematic diagram of torsion pendulum developed by Nielsen[18]. A—Rod attached to fine suspension wire. B—Inertia disk. C—Specimen. D—Specimen clamps. E—Shaft. F—Ball bearings. G—Spring rod. H—Clamps for spring rod. J—Arm carrying core of differential transformer. K—Linear variable differential transformer.



(b)

FIG. 4(b).—Block diagram of electrical equipment used with torsion pendulum; Nielsen[18].

If $\log_e A$ is plotted against the number of oscillations, the slope of the line is equal to λ. Here η is the dynamic viscosity or internal friction, p_n is 2π times the frequency of oscillation and δ is the phase angle previously defined for forced vibrations. Another approximate relation is:

$$\lambda \cong \frac{\Delta W}{2W} \cong \frac{\Delta A}{A} \cong \frac{\pi}{Q} \tag{45}$$

W is the vibrational energy and ΔW and ΔA are the changes in the energy and amplitude, respectively, for two successive free vibrations. Q is a figure of merit for energy storing systems and is used most frequently for electrical oscillating circuits. Another way in which losses are sometimes characterized is by the ratio of the damping to critical damping.

$$\lambda = \frac{2\pi b}{b_c} \tag{46}$$

Here b is the proportionality constant between the damping force and the velocity.

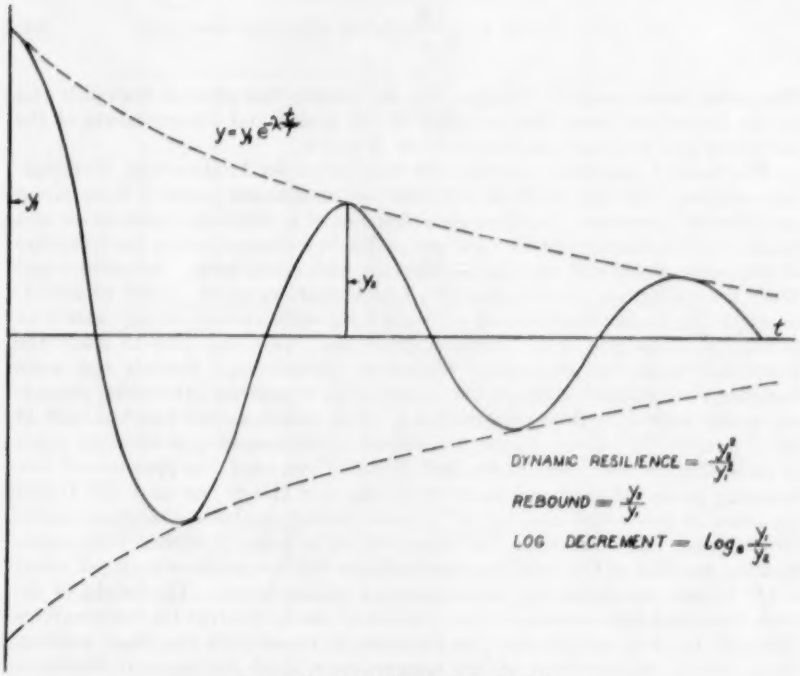


FIG. 5.—Trace of a damped free vibration.

b_c is the above constant for critical damping

$$b_c = 2\sqrt{Mk} = 2M\sqrt{\frac{k}{M}} \tag{47}$$

M is the inertia, the mass or moment of inertia for longitudinal or torsional vibrations, respectively. k is the stiffness, the force per unit displacement or torque per unit of twist, respectively.

The dynamic resilience has been defined as the ratio of the energy in two successive cycles of free vibration. The energy is proportional to the square of

the amplitude so that the dynamic resilience is given by

$$R = e^{-2\lambda} \cong e^{-2\pi p_0(\eta/G')} \cong e^{-2\pi\tan\delta} \cong e^{-2\pi(G''/G')} \tag{48}$$

R is often expressed as per cent rather than as the fraction given by Equation (48).

For pendulum and other rebound tests which involve a deformation process analogous to half a cycle of vibration, the rebound or recovered energy corresponds to the square root of the dynamic resilience. The resilience defined by Yerzley[19] is the fourth root of R or the square root of the rebound.

The period of a freely oscillating, damped system is given by

$$T = \sqrt{\frac{M}{k}(4\pi^2 + \lambda^2)} \tag{49}$$

The period is increased by the damping but usually this effect is negligible and G' can be secured from determination of the period and the constants of the pendulum and test specimen involved in M and k.

The torsion pendulum is especially well suited for fundamental investigations dealing with the effect of structure on mechanical losses. Thus Kuhn and Künzle[17] measured the dynamic properties of a vulcanized gum stock as a function of the static elongation and secured data for investigating the spectrum of relaxation times and making correlations with creep tests. Schmieder and Wolf[8] used a torsion pendulum over a temperature range of −160° to 250° C to study the mechanical-thermal relations for a wide variety of polymers with systematic variations of the chemical structure. This was done to study the molecular causes of mechanical relaxation phenomena. Besides the main damping peak corresponding to the rubber-glass transition, interesting secondary peaks were sometimes resolved, e.g., with unvulcanized butyl rubber at 40° C and 60°–70° C, see Figure 6, ascribed to the loosening of different types of molecular forces. Blanchette and Nielsen[20] reported the presence of two damping peaks for graft polymers of styrene and GR-S, one at −40° C and the other at about 100° C. Ecker[16] showed how the technique might be useful for studying reinforcement. He observed for a natural rubber vulcanizate that the position of the damping maximum on the temperature scale, at about −32° C, was not shifted by the addition of carbon black. The height of the peak decreased with increase in the amount of black, whereas for temperatures above 0° C, as is well known, the damping increases with the black loading. These effects indicate that at low temperatures (high frequencies) the black probably does not exert its characteristic influence in immobilizing and hindering molecular motions and thus increasing internal friction. The low temperature itself accomplishes this. Schmieder and Wolf[8] working with natural rubber gum compounds cured with varying amounts of sulfur found the position of the damping maximum at −50° C to be insensitive to sulfur contents up to 1.5 per cent. At 2 per cent there began a linear displacement of the maximum to higher temperatures. Nielsen and coworkers[20] used a torsion pendulum in studying the relationships between the dynamic mechanical and electrical properties of plasticized polyvinyl chloride compositions and later used such dynamic results to help characterize graft polymers of GR-S and styrene. The grafting shifted the damping peak from −65 or −70° for GR-S to −40° C for one of the graft polymers and in addition a peak appeared at

about 100° C characteristic of polystyrene. The graft polymer acted like a mixture of the two polymers. The polystyrene and rubber segments try to separate from one another and aggregate with themselves. Low temperature properties of elastomers and effects of plasticizers on the low temperature stiffening of natural rubber were studied by Fletcher, Gent, and Wood[15] with a torsion pendulum.

These examples illustrate the type of work for which a torsion pendulum is especially well suited. In addition to the torsion pendulum there have been numerous other types of free vibration devices described and used. The Yerzley oscillograph[19] is well known in rubber technology. Beatty and coworkers[21] used a rubber bushing in a torsional balance type of unit to study time-stress effects at low temperatures and to investigate the dynamic proper-

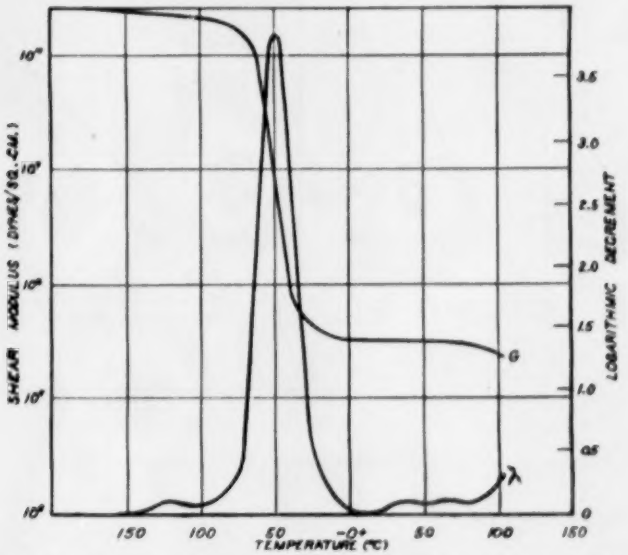


FIG. 6.—Torsion pendulum results for unvulcanized butyl rubber; Schmieder and Wolf[6].

ties of rubber torsion springs. Rorden and Grieco[22] described a horizontally vibrating pendulum for measuring dynamic properties in shear.

Forced vibration, nonresonant methods.—These methods involve direct measurement of the force on the specimen and the corresponding deformation (or velocity). To evaluate the losses, the phase angle between force and deformation may be measured. It should be noted that, as a rule, free vibration methods have inherently greater sensitivity with low loss materials. Thus in a forced vibration method, $\tan \delta$ might be determined but in a free vibration method the quantity measaured is the logarithmic decrement which is $\pi \tan \delta$. The most widely used procedure, especially for methods of technological import, is to record or photograph a hysteresis loop resulting from the accurate mechanical deflections of a stiff series spring or dynamometer, which deflections are proportional to the load on the rubber, and to compound at right angles with this, a motion proportional to the deflection of the rubber. Simple

equations of motion are valid if the wave length of sound in rubber at the driving frequency is much larger than the dimension of the sample in the direction of strain.

Such a hysteresis loop is illustrated in Figure 7(a). Fletcher and Gent[23] have given equations for the ellipse in connection with their work using a forced vibration apparatus with photoelectric pickups and a cathode ray oscilloscope display.

If the applied alternating shearing force is

$$y = S_0 \cos pt \tag{50}$$

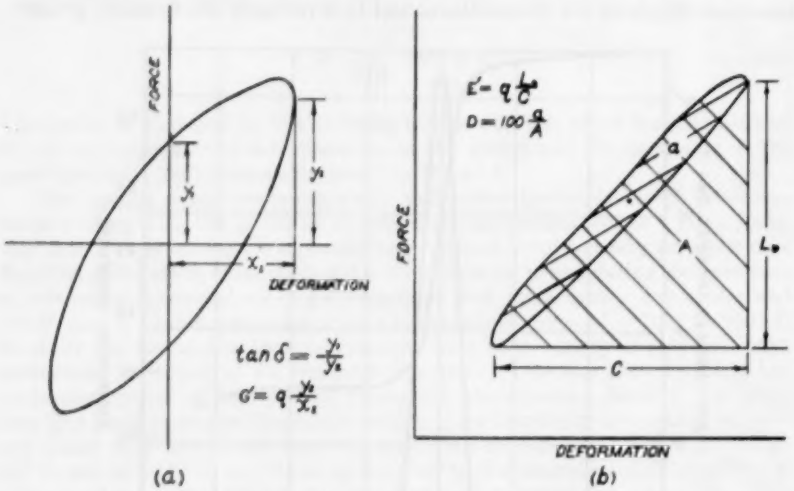


FIG. 7.—Analysis for hysteresis loops traced in forced nonresonant vibrations.

the differential equation of motion is

$$\frac{\eta}{q}\left(\frac{dx}{dt}\right) + \frac{G'}{q}x = S_0 \cos pt \tag{51}$$

where q is a shape factor, h/A, the ratio of the height to the area of the end of the test piece.

The solution of Equation (51) is

$$x = \frac{S_0 q \cos (pt - \delta)}{(G'^2 + p^2\eta^2)^{\frac{1}{2}}} \tag{52}$$

$$\delta = \tan^{-1}\frac{p\eta}{G'} \tag{53}$$

It can be shown that $\tan\delta = y_1/y_2$, where y_1 and y_2 are the ordinates when $x = 0$ and x has its maximum value, x_2, respectively, and that $G' = q(y_2/x_2)$.

The above relations assume the occurrence of a perfect ellipse, i.e., strictly

linear response of the rubber and measuring system. Often there are departures and it has been more general practice[24] not to assume a perfect ellipse but to define the dynamic stiffness as the slope of the axis of the ellipse and the per cent damping as

$$D = 100\frac{a}{A} \tag{54}$$

$$\frac{a}{A} = \frac{1}{2}\pi \tan \delta \tag{55}$$

where a is the area of the hysteresis loop and A is the area bounded by the upper boundary of the hysteresis loop, the minimum load ordinate and the maximum deformation abscissa, Figure 7(*b*). The dynamic resilience as defined for free vibrations is related to D in the following way:

$$R \cong e^{-4D/100} \tag{56}$$

The specific damping capacity is defined as the ratio of the energy loss per cycle to the maximum vibrational energy stored in the sample during a cycle and is

$$\psi = 2\pi \tan \delta \tag{57}$$

η as defined for the free vibration case can be calculated by use of Equations (55) and (48).

The above relations are quite satisfactory if the area of the ellipse is small compared to the area of the triangle under it. But obviously the procedure will not be so satisfactory if the ellipse is relatively large and distorted.

Davies[25] defined resilience as the ratio of the energy output to the energy input per cycle. This ratio depends on the static loading so in general has no simple relationship to R. It is a very undesirable definition for resilience because of this lack of relationship to quantities measured in other test methods. If the static loading is zero

$$\frac{\text{Energy output}}{\text{Energy input}} \cong \frac{A - a}{A} = 1 - \frac{D}{100} = 1 - \frac{\pi}{2}\tan \delta \tag{58}$$

This difference in the definition of resilience was not taken into account by McCallion and Davies[25] in comparing their results with those of others. Thus it is necessary to have reservations in regard to their interesting observation that there is no minimum in the resilience vs temperature curve for rubber if the measurements are made at the same amplitude over the entire temperature range. There is also a question as to whether the measurements were carried to sufficiently low temperatures. At any rate, it is a pertinent inquiry as to what effect the constant amplitude condition might have on the shape of the familiar resilience vs temperature curves.

Nonresonant methods are often designed for wide frequency ranges. The breadth of the dispersion regions for elastomers, regions where the dynamic properties change with frequency, makes a large range of frequencies desirable for many investigations. Experimentally, it is easier to secure a wide range of low frequencies than of high frequencies. Nolle[8,26] used six methods to

cover a range of 0.05 to 10^5 cps in studying the dynamic properties of natural rubber, Buna N, butyl rubber, GR-S, and neoprene over a temperature range from about $-60°$ to $+100°$ C. One of the most interesting observations from these extensive data was that at very low frequencies and sufficiently high temperature (0° C for natural rubber) the modulus increased in proportion to the absolute temperature, the same relation as the kinetic theory of rubber elasticity gives for the equilibrium static modulus. At higher frequencies, the modulus decreased with increasing temperature, the transition occuring at approximately 100 cps for natural rubber and 1 cps for butyl rubber. These results show the dominance at higher frequencies (lower temperatures) of the nonequilibrium, relaxation mechanisms responsible for the dispersion or frequency dependence of dynamic properties whereas at low frequencies there was an approach to the same temperature dependence as for the "static" modulus. Waring[27], with careful measurements, was able to show an increase in dynamic modulus with temperature increase for a natural rubber gum stock.

Philippoff[7], staying below 10 cps, was able to secure about the same frequency ratio as Nolle with a single mechanically driven forced vibrator. The load and deflection of the test piece were indicated by signals from linear differential transformers. The load indication was secured from the minute deflection of a relatively stiff, calibrated spring in series with the test piece. The output from the transducers was fed into a cathode ray oscilloscope and the hysteresis loops recorded photographically. Blizard[28] used an eletromagnetic drive and small shear strains and worked over a frequency range from 0.0125 to 750 cps, a ratio of 1 to 50,000. Jackson, King, and Maguire[28] using two electromagnetically driven vibrators covered a frequency range of about 0.002 to 3500 cps. Davies[25] had available a frequency range from about 5.5×10^{-4} to 25 cps, a ratio of about 1 to 50,000, using direct mechanical recording by means of scratch records which could be enlarged 60 times. When it is kept in mind that such frequency ranges as the above can be extended by the principle of the equivalence of temperature and frequency, it is apparent that forced vibration nonresonant methods are truly characterized by enormous frequency ranges.

There is another type of forced nonresonant procedure, sometimes referred to as the transducer method, which has been highly developed and used principally for basic research investigations over wide ranges of frequency and temperature at low amplitudes[29]. The mechanical impedance is measured in terms of electrical circuit elements. An electromagnetic transducer, i.e., a coil in a magnetic field through which alternating current of controlled frequency passes, provides the driving force. The electrical and mechanical impedances enter into the equations for the system. Measurements of the resistance and reactance of the coil by bridge circuits when it is clamped and when it is in motion provide data for computing the mechanical impedance and hence the dynamic properties. Later, a second coil was added, an arrangement known as a twin transducer, see Figure 8. One coil served as the driver and the other as the pickup. The open circuit voltage from the pickup coil was compared in amplitude and phase with the driving current by bridge circuits. Or, alternatively, driving current could pass through both coils. Measurement of the impedance, the ratio of voltage to current for one coil for two different ratios of the two driving currents eliminated the need for measurements on a clamped coil. The frequency range was about 25 to 5000 cps with temperature control from $-50°$ C to $+150°$ C.

The torsion pendulum described and used by DeWitt and coworkers[30] illustrates the interest in overcoming, the frequency limitations inherent in a freely oscillating device. The pendulum could be used in free vibration or it could be driven by means of variable but controlled frequency alternating current passing through a coil suspended in the field of a permanent magnet so that frequencies from any practical lower limit up to 15 cps could be used. The relative amplitude of the driving force and the response determined the dynamic stiffness and the mechanical phase angle between them determined the energy loss. The method of measurement involved the use of two light beams, one reflected from a mirror on the coil and the other from the mirror of a galvanometer through which the driving current also passed. The phase differency between these beams, which is the phase difference between the stress and strain in the sample, was measured by means of a suitable arrangement of photocells and a recorder. Moduli from 10^5 to 10^{10} dynes/sq. cm could be measured over a temperature range of $-80°$ C to $+100°$ C. The lower limit for loss factor measurements was about 0.1. For lower values than this, operation as a free pendulum was preferable. No provision appears to have

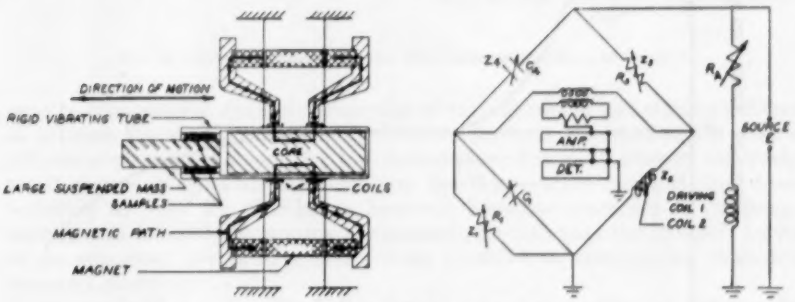


FIG. 8.—Schematic diagram and circuit for twin transducer, nonresonant method of Fitzgerald and Ferry[29].

been made for assuring that there was no longitudinal static stress in the samples.

The usefulness for such a precision research device is illustrated by the comparison which was carried out of the dynamic properties of unvulcanized natural rubber and GR-S. In general, the characteristic dependence of the modulus of uncrosslinked, amorphous polymers on temperature or frequency is shown in Figure 9. For high frequencies or low temperatures, they are rigid with moduli of the order of 10^{10} dynes/sq cm. As the frequency is lowered or the temperature raised, a transition region is entered where the modulus drops rather abruptly to 10^6–10^7 dynes/sq cm. Thereafter there is a plateau attributed to the chain entanglements. Consequently, the length of this plateau depends upon the molecular weight. Beyond this plateau, upon progressive lowering of the frequency or raising the temperature, the polymer becomes softer and more plastic. The above pattern of behavior is very common, differences occurring in details such as the height and length of the plateau, the temperature ranges, etc.

The comparison which was made of GR-S and natural rubber was limited to high molecular weight fractions. The molecular weight distribution of GR-S is known to be quite important for its dynamic properties. At any rate, for

the high molecular weight fraction, there was a very close similarity in the dynamic behavior of the two polymers. Natural rubber had a more abrupt glass transition region at a lower temperature than GR-S. The modulus in the rubbery plateau region was higher for GR-S than for natural rubber. The complete molecular weight distribution in GR-S would have the effect of shortening the plateau and increasing its slope. To secure a useful rubber, it is necessary to stabilize the plateau and extend its length by crosslinks. As previously explained, the slope of such a dynamic modulus curve is a measure of the mechanical losses. Zapas, Shufler, and De Witt[30] considered that the modulus due to crosslinking GR-S by vulcanization was of necessity too low compared to the plateau modulus so that one of these moduli dominates in one frequency region and the other in a different frequency region, a modulus dispersion situation which leads to increased dynamic losses and heat generation.

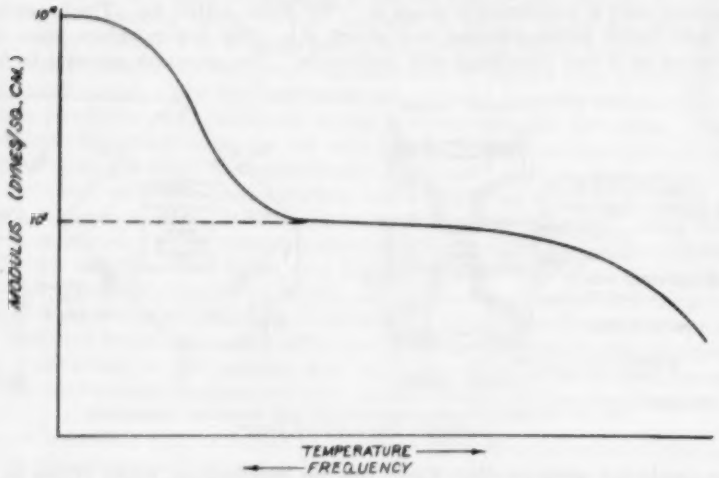


FIG. 9.—Characteristic dependence of modulus on frequency or temperature for an amorphous, uncrosslinked elastomer. The plateau is attributed to the stabilizing effect of molecular entanglements; the rise at low temperatures (high frequencies) to intermolecular, secondary valence forces and the drop off at high temperatures (low frequencies) to slipping of the molecular entanglements, i.e., plastic flow.

Nonresonant methods have also been widely used for technological investigations of the dynamic properties of rubber. Painter[31] developed a vector subtraction method for measuring dynamic properties which avoided the recording of hysteresis loops and which was applicable for very low losses, for tan δ as low as 0.003. The unit was driven mechanically with controlled, variable amplitude and had a frequency range of 15–60 cps. Strain gages were used to measure both the alternating force and displacement by means of a bridge circuit, the output of which was read with a vacuum tube voltmeter. The displacement pickup was mounted on a beam of circular section which could be rotated to provide a voltage signal of adjustable amplitude which opposed or nulled out the portion of the voltage generated by the in-phase component of the force. The minimum voltage signal from the bridge was then proportional to the out-of-phase or damping force component. The principles of the method are illustrated in Figure 10. The equipment was

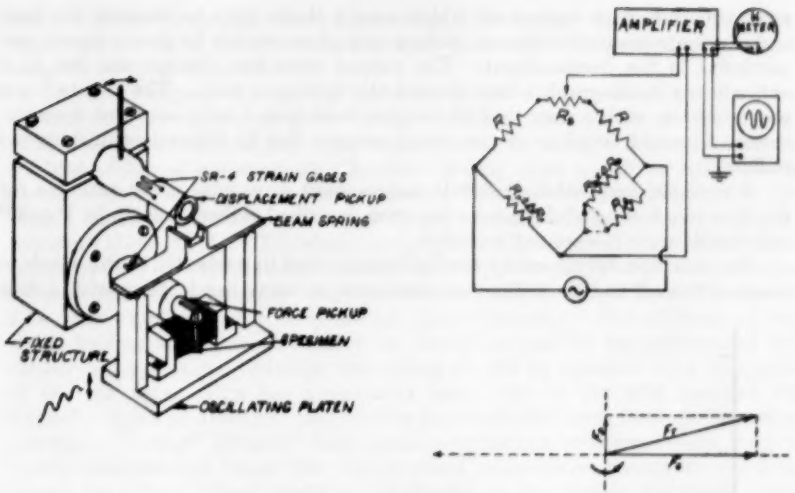


FIG. 10.—Schematic diagram for the vector subtraction method of Painter[21].

used to compare the dynamic properties of natural rubber and silicone rubbers of interest for vibration isolators. Noteworthy was the observation that a silicone compound designed for low temperature flexibility showed relatively small change in dynamic modulus over the temperature range studied from −100° F to +80° F. The losses, however, increased markedly as the temperature was reduced, illustrating the general principle that the dynamic losses of an elastomer are usually much more sensitive to temperature than the dynamic modulus.

Schmuckal[22] has described the forced vibration testing of automobile

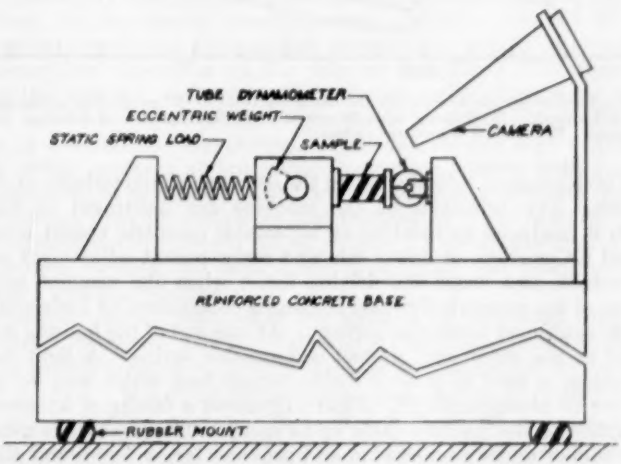


FIG. 11.—Schematic diagram of Roelig machine; Roelig[24].

engine mounts with equipment which used a strain gage to measure the load and an electromagnetic velocity pickup and phase shifter to give a signal proportional to the displacement. The output from the pickups was fed to a cathode ray oscillograph which showed the hysteresis loop. The driving force was varied in such a way that all mounts were tested with constant dynamic energy to avoid favoring or penalizing mounts due to differences in dynamic stiffness.

A versatile and rather elaborate nonresonant sinusoidal strain machine for the dynamic testing of elastomers has been described rather recently by Payne[33] but results with it were not included.

The machine developed by Roelig[24] contributed importantly to the development of Buna S and since then has continued, in many hands, to provide a flow

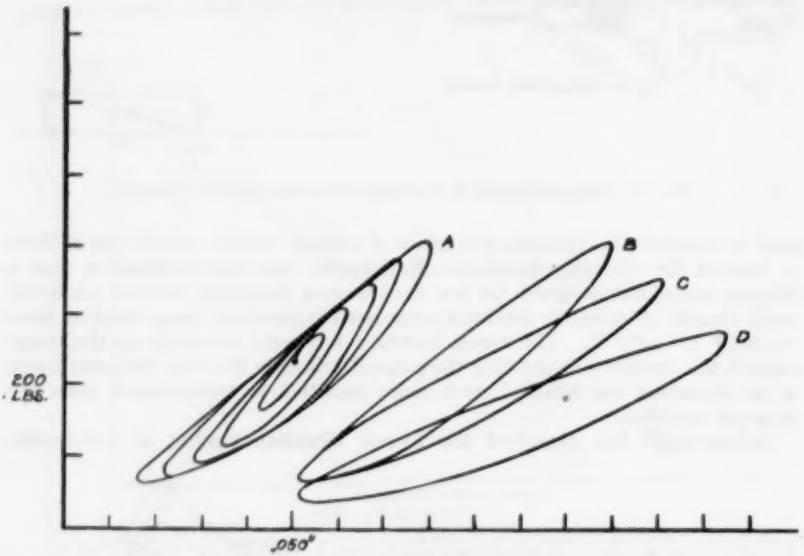


FIG. 12.—Hysteresis loops secured with the Roelig machine; A—When starting up the machine, running time 0-3 seconds. B—Running time, 30 seconds. C—Running time, 2 minutes. D—Running time, 5 minutes. Results of Wilkinson and Gehman[34].

of useful technological information on the dynamic characteristics of elastomer compounds. The principles of the machine are illustrated in Figure 11. Vibration is produced by rotating an adjustable eccentric weight with a variable speed DC motor. A spiral cam and screw permit adjustment of the eccentric weight, and hence the driving force, when the machine is running. Oscillation of the eccentric flywheel housing is constrained to horizontal motion by flexible cantilever mounting springs. At one end of the housing is the testpiece and at the other end, a steel compression spring. A light beam and mirror system is used to project the hysteresis loop which may be manually traced over or photographed[24]. Figure 12 shows a family of hysteresis loops photographed as the machine came up to speed. The machine is usually used with the rubber under compression and provides larger forces and amplitudes than most of the equipment heretofore described. The frequency range is

about 0.01 to 20 cps, the static load range 5–20 kg/sq cm, and the dynamic load range 4–18 kg/sq cm. Results have been reported over a temperature range of −40° C to +150° C.

Payne[35] claimed that second harmomics and consequent distortion were evident in hysteresis loops given by the Roelig machine. He carried out an extensive mathematical and experimental analysis for the second harmonic content of forced nonresonant vibrations arising from nonlinear stress-strain characteristics of rubber in compression. The operating conditions for the Roelig machine and others of similar character can and should be arranged to minimize these effects. The shape factor, ratio of load area to free area, of the testpiece used by Payne was unfavorable. The nonlinearity of the compression stress-strain curve becomes more pronounced as the shape factor increases. Low static and dynamic compressions favor linearity. The stiffness of the static loading spring should match as closely as possible the stiffness of the rubber test specimen. Ideally, this spring should be replaced by a duplicate of the testpiece. This has apparently been done in the new machine by Payne[33]. Such an arrangement provides an essentially linear force-deformation relation. Waring[36] obtained fairly good correlations between results with a Roelig machine and those with an electrical compression resonance vibrator except for effects which could be attributed to the higher amplitudes and energy input of the Roelig machine. Under good operating conditions excellent correlations can be obtained between results from the Roelig machine and those from a resonance vibrator[34].

Recent investigations of Ecker[16,37] and others illustrate the capabilities of the Roelig system and areas of dynamic testing and research for which it is well suited. Equipment was developed for studying dynamic properties in tension. Three dimensional contour maps were constructed to show the damping and spring constant as functions of elongation (20–180%) and temperature (−50°–+120° C). The dynamic amplitude was relatively small compared to the static elongation, about 2–5%. The frequency was 25 cps. With almost every polymer, damping decreased with static elongation. Vulcollan, however, was an exception and showed an increase in damping at higher elongations. An unexpected minimum was generally observed for the dynamic spring constant at intermediate elongations, usually between 60 and 100% elongation, depending on the polymer and filler. The interpretation given for this was that molecular orientation at higher elongations more than offset the breakdown of weak bonds responsible for the decline of the dynamic modulus at intermediate elongations. Vulcollan showed high values for the dynamic spring constant at low static elongations, demonstrating an apparently high degree of thixotropy in the decline in stiffness at higher elongations.

Compression dynamic tests were used to investigate and compare reinforcement characteristics of different fillers. Figure 13 illustrates the type of contour map used to show the dependence of damping and spring constant on temperature and filler loading.

Damping curves as a function of temperature for elastomers such as Perbunan, Buna S, neoprene, and butyl showed a sharp maximum the position of which was specific for each material and served to characterize its low temperature performance. Nearly all of the polymers showed in addition more or less pronounced secondary maxima. Buna S and Buna SS gave characteristic secondary maxima between 60° and 100° C which occurred independently of the composition of the compound. Vulcollan showed low damping only in a

narrow temperature range, 40°–50° C. and secondary maxima which were better developed by static prestressing.

Such secondary softening regions and damping maxima gave interesting possibilities for differentiating between copolymers, polymer mixtures, and graft polymers. Thus, in mixtures of polystyrene and natural rubber, the polystyrene did not displace the primary damping maximum but a strong secondary maximum due to the polystyrene appeared at 120–130° C. Blends of natural rubber with high styrene-butadiene copolymers gave interesting damping curves. Again, the position of the primary maximum was unaltered but, for the same sytrene content in the compound, the position of the secondary maximum was at about 90° C with a 90/10 styrene-butadiene resin and at about 55° C with a 70/30 resin. The damping curve for a commercial graft polymer of natural rubber and methyl methacrylate did not distinguish it from

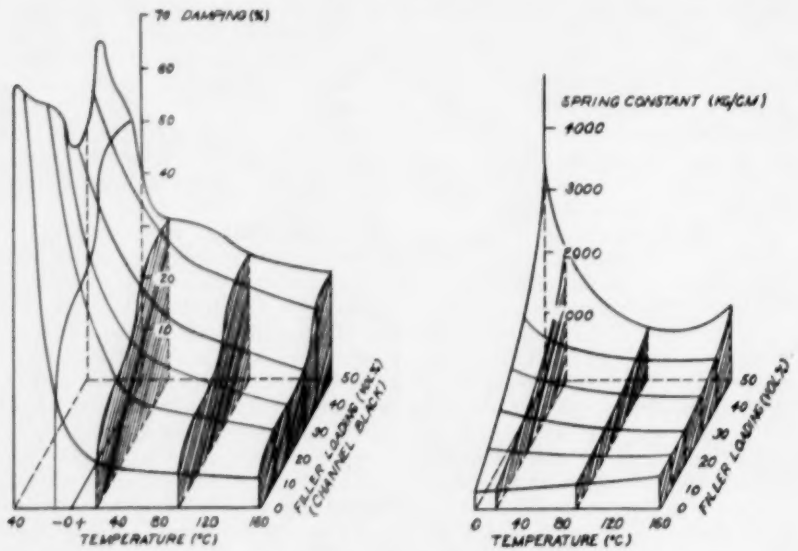


FIG. 13.—Illustration of contour presentation used by Ecker[87] to show the dependence of dynamic properties on filler loading and on the temperature.

mixed polymers prepared by blending latices of the two polymers as far as the position of the secondary maximum was concerned. However, the graft polymer had notably lower damping than the mixtures over the range of temperatures used. Peter and Heidemann[87] have recently described an adaptation of the Roelig system for following the course of vulcanization continuously by measurement of the dynamic modulus during cure.

As a further illustration of the usefulness of dynamic measurements for characterizing the properties of rubber compounds and the assistance they can give in technological developments, may be cited a few results recently reported by Zapp[88] indicating how the relative damping and dynamic modulus of a butyl tread compound could be markedly reduced by special processing although the conventional static 300 per cent modulus was actually much higher.

Forced vibration resonant methods.—Forced vibration resonant methods are based on the response of a tuned mechanical system, some or all of the stiffness of which is due to the elastomer, when the applied driving frequency is in the vicinity of the natural resonant frequency, that is, the frequency if the system were vibrating freely. In general, the dynamic modulus affects the resonant frequency; the losses affect the breadth of the resonance peak and determine the driving force required to attain a given amplitude at resonance.

The forced resonant vibration of a cantilever reed or strip of the elastomer clamped at one end has been used to study dynamic properties in several instances. Nolle[26] investigated the possibilities of the method, driving the clamped end with a phonograph recording head and observing the amplitude of the end of the reed with a low power microscope. The reed dimensions were 1.7 cm length, 0.08 cm thick, and the half amplitude of vibration at the tip was about 0.025 cm. The frequency range was 10–500 cps. The limitations of the method were found to be rather severe but it was considered to be useful

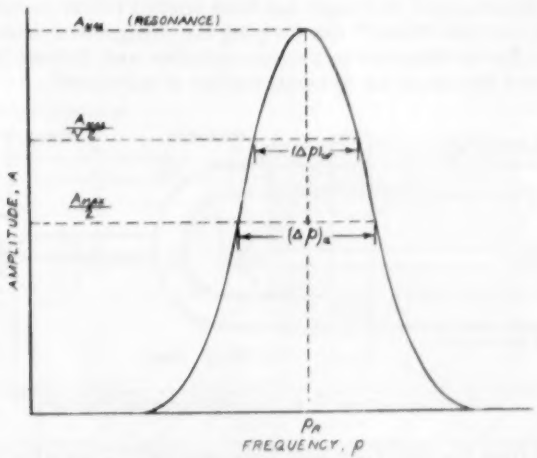


FIG. 14.—Diagram of resonance peak secured with forced, resonant vibration methods.

for studying the temperature dependence of the dynamic modulus. Sack, Motz, Raub, and Work[29] employed several variations of a reed technique in which the free end was driven by electrical forces, or, for longitudinal vibrations, by the electromagnetic force on an attached coil carrying alternating current in a magnetic field. Photoelectric cells were used in connection with appropriate circuits and a cathode ray oscilloscope to observe the vibrations. The damping of free vibrations of the reed could also be measured with the equipment and, in another variation, the area of a hysteresis loop on the cathode ray screen served to determine the losses. The frequency range covered by all these possibilities was about 20–3500 cps. Observations on natural rubber were generally consistent with those reported from other forced resonance methods.

The characteristic way of specifying the losses for a vibrating reed experiment is analogous to that used for an oscillating electric circuit. The amplitude of vibration is plotted as a function of the driving frequency and the

width of the resonance peak furnishes a convenient measure of the losses, see Figure 14.

$$\frac{(\Delta p)_w}{p_r} = \frac{(\Delta p)_a}{\sqrt{3}\, p_r} = \frac{1}{Q} = \tan\delta = \frac{E''}{E'} \tag{59}$$

p_r is the natural resonant frequency of the reed at which the amplitude is a maximum. $(\Delta p)_a$ is the breadth of the peak at two points where the amplitude of vibration is one half of the amplitude at resonance. $(\Delta p)_w$ is the breadth of the peak where the power is down by half, i.e., where the amplitude is $1/\sqrt{2}$ times the maximum amplitude.

Calculation of the dynamic modulus, E', from the vibrating reed experiment involves the mathematical analysis for flexural vibrations and approximate solutions have usually been used[15,26,39]. The vibrating reed method is probably inherently better adapted for metals and rigid plastics and has been more widely used for such materials than for elastomers. However, an adaptation of the vibrating reed technique has been applied rather recently by Bopp, Kirkland, Sisman and Towns[40] for studying the changes in dynamic properties of elastomers due to exposure to nuclear radiation and Nohara has also used a vibrating reed technique for dynamic studies of polymers[40].

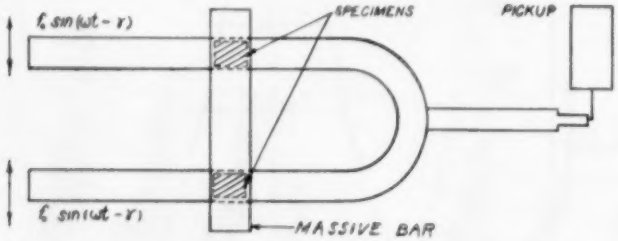


FIG. 15.—Schematic diagram for tuning fork arrangement for measuring dynamic properties as developed and used by Rorden and Grieco[22] and Hopkins[41].

A method from the Bell Telephone Laboratories[22,41] illustrates the principles involved for measuring the dynamic modulus and losses for elastomers by determining the effect of the elastomer on the resonant frequency and breadth of the resonant peak of a tuning fork system subjected to forced vibrations at frequencies in the vicinity of its natural resonance frequency. A schematic diagram of the arrangement is shown in Figure 15. The method was used to measure dynamic properties in shear for frequencies in the acoustic range, 100–6000 cps. It has the feature of using two quite small samples 0.20 × 0.25 inch and from 0.010 to 0.031 inch thick. Of course, such small samples are probably not advantageous from the standpoint of precision.

The tuning fork was driven at the two ends by two electromagnetic telephone receivers and a variable frequency oscillator. The vibrations were picked up by means of a piezoelectric crystal pickup so that plots of amplitude vs frequency could be obtained. The two specimens were placed between the tines of the fork and a fixed bar as indicated in Figure 15. Accurate determination was required of the change in frequency and change in breadth of the resonance peak caused by the specimens. The stiffness and losses of the specimens could then be calculated. The calculations assumed the fork to be

equivalent to a simple mass-spring-viscosity system and the added impedance of the elastomer to be a series stiffness and viscosity. Such calculations are facilitated by consideration of analogous electrical circuits. Dynamic properties over the frequency range and for several temperatures were published for butyl rubber, natural rubber, and silicone rubber compounds as well as for PVC and other plastics.

The magnetostriction method of Nolle[26] was based on similar principles and was adapted to determine dynamic properties in compression for a frequency range of about 10 kc to 100 kc. Longitudinal vibrations were excited in a metal rod. The small change in resonant frequency when the rubber sample was pressed against the end of the rod was related to E' for the sample and the change in width of the resonance peak was related to E''.

The most extensively used forced vibration resonance methods with elastomers include a vibrating system for which the elastomer provides essentially all of the stiffness and damping. The stiffness and damping of auxiliary mount-

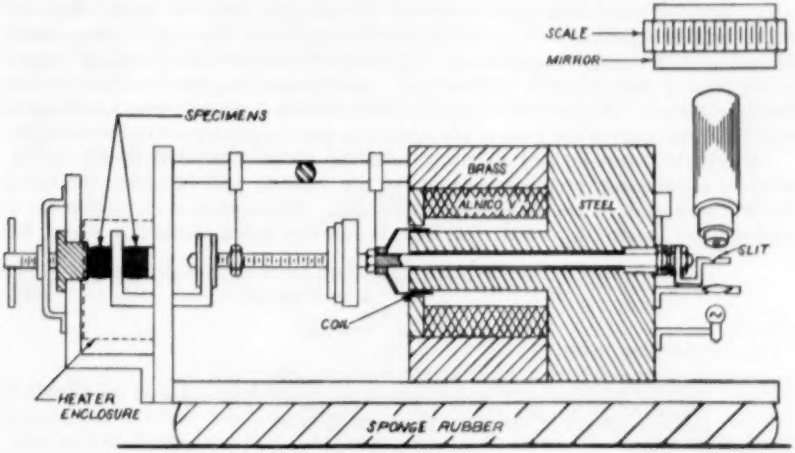


FIG. 16.—Schematic diagram for an electromagnetic forced resonant vibrator (Goodyear Vibrotester).

ing springs, if not entirely negligible are taken into account by small corrections. Such systems are brought into resonance with the driving force by variation of either the vibrating mass or the driving frequency. They have been driven by the alternating force set up by rotating eccentric masses[42]. In this case, there is a tie-in between the magnitude of the driving force and the frequency, which is usually undesirable. More flexibility in this respect resides in driving the system with the electromagnetic force on a coil carrying alternating current of controlled frequency in a magnetic field. This has been the preferred arrangement. Many systems of this sort have been described and widely used for systematic studies of various aspects of the dynamic behavior of rubber compounds[42]. A schematic diagram for such equipment is given in Figure 16. Although lacking in range of frequency in comparison with forced nonresonant methods, the maximum range is usually about 5–300 cps, these tuned systems are especially well adpated for technological purposes of compound

and polymer development and testing laboratory operation. As with many other methods, the frequency limitation can be overcome to some extent by measurements over a range of temperatures. At low temperatures, however, the resonance peaks become broad, exact tuning is difficult and precision suffers. The same circumstance limits the accuracy of the measurements with high loss materials. The amplitudes have been measured by direct observation with a measuring microscope, projection of a slit image, electrical pickups and photocells. Waring[27] employed phase tuning, which takes advantage of the fact that at resonance there is zero phase difference between the mechanomotive force and the velocity. But usually tuning is accomplished by adjusting the mass or frequency to secure maximum amplitude. The facility with which the amplitude can be controlled and the range of amplitudes are characteristic advantages of these methods, which have furnished nearly all of the data on the dependence of dynamic properties on amplitude. Equipment of this nature has been described for vibrating rubber in shear, in compression, or in either way. For purposes of comparing dynamic properties of vulcanized compounds or polymers, either shear or compression may be used. But for unvulcanized material, a shear test is usually preferable because of permanent set induced by static compression. Angioletti[42] used a rubber ring of trapezoidal cross section bonded to inner and outer metal rings and oscillated it in torsional shear. Photoelastic analysis showed that a given shear strain gave uniform stress only if the base of the specimen was long compared to the height.

Although unsatisfactory in many respects, linear vibration theory which assumes a damping force proportional to the velocity still furnishes the basis for interpretation of the dynamic test results. The equation of motion for a rubber-mass system in forced vibration, the rubber being stressed in shear, is:

$$m\frac{d^2x}{dt^2} + \frac{\eta}{q}\frac{dx}{dt} + \frac{G'}{q}x = F\cos pt \qquad (60)$$

m — vibrating mass, grams
x — displacement from equilibrium position, cm
η — internal friction or dynamic viscosity, dynes/cm/sec
q — ratio of height of testpiece to the load area, cm^{-1}
t — time, sec
F — maximum value of driving force (dynes)
p — angular frequency (radians/sec)

The equation has the same form for vibration under compressive stress. The values of η and E in this case will be independent of the size of similarly shaped testpieces but, as in static tests, E and likewise η, will depend on the shape, i.e., the ratio of load to free area[42]. Morris[44] has suggested the use of scaled down models for the development of rubber mountings on the basis of satisfactory experiments with scaling factors. The ratio η/E determined under comparable conditions of temperature, amplitude, frequency etc. tends to a first approximation to be a material constant independent of whether shear or compression vibrations are used, especially if the ratio of load area to free area is small. Payne[45] has achieved further generalizations in regard to the effect of shape on the dynamic properties of rubber in compression.

The dynamic shear properties G' and G'' are expected to be related to E' and E'' for compression or tension stress in approximately the same way as in the static case, i.e., assuming incompressibility of the rubber, they are one-third as large. But this relation only holds if Young's modulus is independent

of the shape of the specimen, that is, if the ends are lubricated or the free area is large compared to the load area. Superposed static stresses affect the dynamic values and disturb the "ideal" relationship between shear and compression values. Superposed static compression increases E' and E'', the results being referred to the original dimensions. The effects of superposed static shear and compression on G' and G'' reported by Fletcher and Gent[42] are rather involved, depending on the type of compound.

Oberto and Palandri[42] had a favorable arrangement for securing results which were independent of sample size and shape and superposed compressive stress. The testpiece was a rubber ring between metals and was vibrated in torsional shear. Reduction of edge effects by use of a ring sample was considered to be the decisive factor in these results. The theoretical ratio of 1:3 was secured between dynamic shear modulus and the dynamic tension modulus for rubber bands of various sizes oscillated longitudinally. Incidentally, in this work, there was observed a minimum of hysteresis and modulus as a function of static elongation in the range from 70–130% depending upon the compound. This is in agreement with the forced nonresonant results of Ecker[16] already discussed. De Meij and van Amerongen[43] working with samples in compression showed that when E' was plotted as a function of shape factor, the curve extrapolated to $3G'$ for zero shape factor. They found that E' and E'' depended upon the shape in the same way so that the loss factor E''/E' was independent of shape.

The steady state solution of Equation (60) is

$$x = \frac{Fq \cos (pt - \theta)}{\sqrt{(G' - mqp^2)^2 + \eta^2 p^2}} \tag{61}$$

The phase angle between force and displacement is

$$\tan \theta = \frac{\eta p}{G' - mqp^2} \tag{62}$$

It should be noted that θ is the phase angle between the driving force on the system, not the force on the rubber, and the displacement and hence is not the same as δ of Equations (27), (43) and (53). Tan θ has the inertia term mqp^2 in the denominator and tan δ does not. As in the case of nonresonant forced vibration, an elliptical hysteresis loop is generated by a trace of driving force vs deformation but it is not the same loop as occurs for nonresonant vibration. At resonance, θ is 90°. Equation (62) reverts to Equation (53) if the mqp^2 term is small compared to G'.

Moyal and Fletcher[42] have provided comforting reassurance that free vibration and forced resonant vibration results are consistent. The same testpieces were excited both by passing pulses through the coil to record damped free vibrations and alternatively in the usual way to produce forced resonance vibrations. Resilience values from both procedures agreed quite well.

The magnification factor is defined as the ratio of the maximum amplitude of vibration for a given amplitude of driving force, F, to the static deflection produced by a force F. It depends on the ratio of the frequency of the driving force to that of the undamped natural frequency of the system. When these are equal, i.e., at resonance, the magnification factor is given by:

$$M.F. = \frac{\sqrt{qmG'}}{\eta} = \cot \delta \tag{63}$$

The magnification factor for rubber compounds in this type of equipment usually falls in the range from about 10–30. This shows the advantage of a forced resonant system in being able to produce much larger amplitudes of vibration with a given driving force than could be produced by direct application of the force to the rubber.

To a close approximation, if the damping is not too large, the maximum amplitude as the mass or frequency is varied occurs when

$$G' = mqp_0^2 \tag{64}$$

and then

$$x_0 = \frac{Fq}{\eta p_0} = \frac{Fq}{G''} \tag{65}$$

The zero subscript is for resonance values. The relationships of η, G', and G'' to the logarithmic decrement and the resilience defined for free vibrations have been given in Equations (42), (43), and (48). The symbols G' and G'' have been retained although it should be kept in mind that they were originally defined for vibrations of small amplitude in the linear range.

One of the most useful applications for dynamic measurements is the estimation they permit of the relative heat generation. The energy loss, or heat generated in the specimen per cycle of amplitude X is

$$H_x = \pi p X^2 \frac{\eta}{q} \tag{66}$$

For shear vibrations, the heat generated per unit volume per cycle is

$$H = \pi \epsilon_0^2 G'' \tag{67}$$

where ϵ_0 is the amplitude of the shear strain.

The rubber does not know or care if it is being vibrated resonantly or nonresonantly and generates this same amount of heat regardless of the type of apparatus. If a cyclic force of amplitude F is applied directly to the rubber, the inertia of which is negligible

$$X = \frac{Fq}{G'} \tag{68}$$

And the heat generated in the specimen per cycle is

$$H_f = \pi p \eta q \frac{F^2}{G'^2} = \pi q F^2 \frac{G''}{G'^2} \tag{69}$$

Approximate relations for H_f and H_x, sometimes useful for securing relative values, are given below:

$$H_x \propto (100 - R) G' X^2 \tag{70}$$

$$H_f \propto \frac{(100 - R) F^2}{G'} \tag{71}$$

Equations (70) and (71) become progressively inaccurate as R decreases. R is the dynamic resilience defined by Equation (48). One of the most severe

practical limitations for the direct application of these equations is the uncertainty in how to suitably characterize complex deformations such as occur in tires, for instance. This is a field in which work could profitably be done to make dynamic measurements more useful. Figure 17 illustrates the opposed course of H_x and H_f trends as filler loading is increased. G'' or ηp is usually nearly independent of frequency in the mechanical range of frequencies for most elastomers. This implies that the resilience, Equation (48), the amplitude at resonance for the same driving force, Equation (65), and the heat generation per cycle, Equations (66) and (69), will not depend much on frequency in this range. Fletcher and Gent[42], for widely different compounds, found ηp^c to be constant, c being in the range from 0.70 to 0.95; Dillon, Prettyman, and Hall[43] found the range to be 0.78 to 1.0, including results with different polymers. It is important in evaluating the effect of frequency on G' and G'' to avoid confusion between effects of frequency and of amplitude. As the frequency is

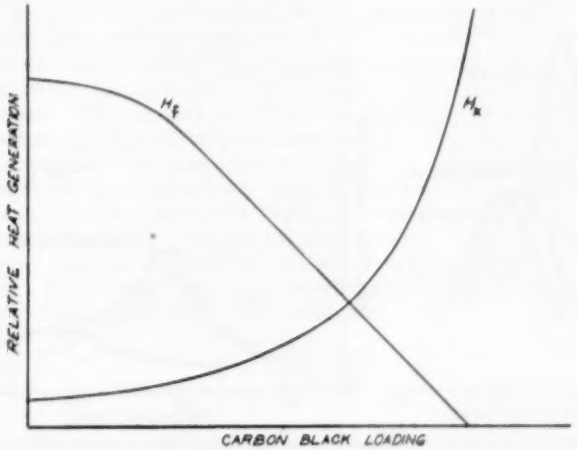


FIG. 17.—Comparison of the effect of filler loading on heat generation for constant force and constant amplitude vibrations. The effect of filler loading on the modulus dominates the course of the H_f curve; as the filler loading is increased, the deflection for a given amplitude of the driving force decreases and relatively less heat is generated.

raised the power of the equipment being limited, there is a tendency to work with smaller amplitudes whereas the determinations should presumably be made at the same amplitude if the amplitude is out of the linear range. η and G' tend to increase with decrease in amplitude so that a rise of ηp and G' with frequency is the course anticipated if they are actually invariant with frequency but the testing amplitude at higher frequencies becomes progressively smaller. Many of the results reported for such studies do not state if the amplitude at resonance was constant for all the frequencies. In the above work, however, the modulus was reported to be constant over the frequency range so that the indicated dependence of ηp on frequency is no doubt a true frequency effect. Oberto and Palandri[43], however, found the calculated hysteresis losses to be proportional to frequency, implying the constancy of ηp.

As a few examples of the type of work for which resonant forced vibration methods are well suited, may be cited the dynamic study of reinforcement by

Waring[37]; study of the relationships between the dynamic properties of raw and vulcanized polymers by Enabnit and Gehman[42] and the more recent technological investigation of the dynamic mechanical characteristics of rubber compounds by de Meij and van Amerongen[43].

Waring observed that the temperature variation of the dynamic modulus for tread stocks was in the opposite direction to that for the equilibrium static modulus as given by the kinetic theory of rubber elasticity, indicating the importance of interaction forces related to reinforcement. The energy of activation from the temperature dependence of the dynamic modulus for tread stocks was low, of the order of 0.5 to 2 kcal, showing that weak cohesive bonds are responsible for the variation of dynamic modulus with temperature. This variation with temperature, as well as the variation with amplitude, were suggested as criteria of the strength of cohesive bonds in reinforcement. The work was augmented by observations of temperature and amplitude induced

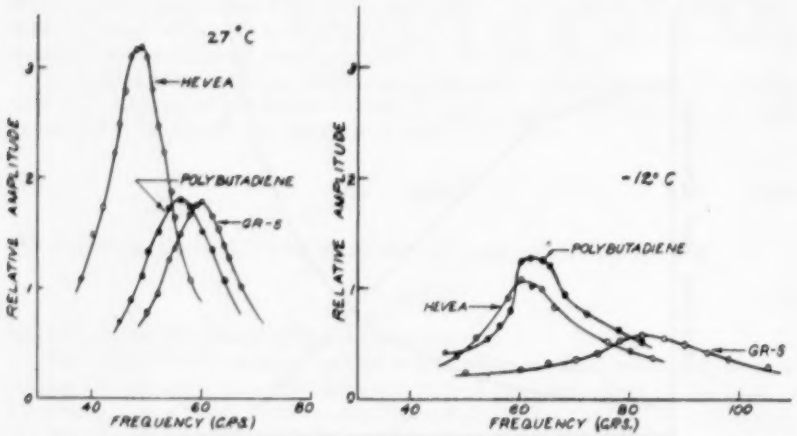


FIG. 18.—Effect of temperature on resonance curves secured for tread compounds with a forced, resonant vibration system (Goodyear Vibrotester). The relative amplitude plotted as ordinate is proportional to the amplitude (cm.) per ampere of driving current.

changes in electrical conductivity in correlation with changes in dynamic properties.

Enabnit and Gehman were able to trace a correlation between the dynamic properties of a series of raw polymers and those of vulcanized gum and tread compounds prepared from them and followed the progressive changes in dynamic properties from the raw to the overcured state. The dynamic modulus and resilience for raw GR-S type polymers were practically independent of the Mooney plasticity for any one polymer but showed differences in level corresponding to the quality of the polymer. For raw natural rubber, however, the resilience falls with progressive milling. Resilience for a raw polymer decreases at elevated temperatures where that for the cured polymer is still rising. de Meij and van Amerongen struggled with the difficulties in measuring dynamic properties at low temperatures with a resonant method and observed the maximum in the loss factor near the second order transition point for natural rubber, cold GR-S, Vulcollan, and butyl rubber. Two maxima were shown for a compound reinforced with a styrene-butadiene resin, one being at 80° C. Heat

treatment of butyl rubber containing 50 parts EPC black decreased the loss factor at elevated temperatures and gave low dynamic moduli at low amplitudes. Reinforcement of natural rubber with Aerosil and with aniline resin gave low values for the loss factors. Thiuram vulcanizates had high losses.

Figure 18 shows the effect on resonance curves secured with the Goodyear Vibrotester of reducing the temperature from 27° C to −12° C. At −12° C the resonance curve for the GR-S tread compound was very broad. The internal friction is much more sensitive to temperature than is the dynamic modulus. Thus the amplitude at resonance was affected more by the temperature reduction than was the position of the curve on the frequency scale. Data taken by Stambaugh[42] for a natural rubber tread compound showed that reduction of the temperature from 120° C to 0° C caused the dynamic modulus to increase by a factor 1.67 whereas η increased by a factor of 5.50.

Propagation methods with continuous waves.—Dynamic properties in the acoustic range of frequencies have been investigated by wave propagation methods. A variety of elastic waves may be propagated in rubber depending upon the excitation and the geometry of the testpiece. Thus longitudinal, torsional, or flexural waves may be propagated along a strip or rod. For a viscoelastic material, energy is absorbed from the wave so that it is attenuated as it progresses. The dynamic properties can be related to the wave propagation parameters, i.e., the velocity and attenuation. Practically all of the work with elastomers based on measurements of velocity and attenuation of waves along a strip have been carried out with longitudinal waves. Nolle[26] has described the method and given the applicable equations. The strip must be small in cross section as compared to the wave length. The dynamic properties are connected with the propagation measurements by solution of the wave equation for a plane longitudinal wave assuming a frictional force proportional to the rate of change of strain. The results are

$$E' = \frac{\rho c^2 (1 - r^2)}{(1 + r^2)^2} \tag{72}$$

$$E'' = \rho c^2 \frac{2r}{(1 + r^2)^2} = \frac{2rE'}{1 - r^2} \tag{73}$$

r is a dimensionless parameter, given by

$$r = \frac{L\lambda}{54.6} = \frac{\alpha c}{p} = \frac{\alpha \lambda}{2\pi} \tag{74}$$

λ is the wave length, L is the attenuation in decibels/cm, that is, $L\lambda$ is the attenuation in db per wave length. Acoustic attenuation is frequently expressed in nepers/cm. An attenuation of one neper corresponds to a reduction of the wave amplitude by a factor of e^{-1}. If the acoustic attenuation in nepers/cm is α, then $L = 8.68\,\alpha$. The maximum value of r is unity. c is the phase velocity, ρ the density and p the angular frequency.

Actually, Equations (72) and (73) are of a general form and can serve to calculate the components of the appropriate complex dynamic modulus for any type of wave in a viscoelastic medium. The equations have been used for shear waves[46] in which case G' and G'' are obtained. For bulk waves, the applicable composite modulus is $K' + \frac{4}{3} G'$. K' is the real part of the bulk modulus. The composite viscosity for bulk waves is $K'' + \frac{4}{3} G''$.

The experiments with longitudinal waves have usually been carried out[26,47,48] by vibrating one end of the rubber strip longitudinally by connecting it to a crystal unit or similar transducer driven by an electrical oscillator. A vibration pickup unit is moved along the strip so that the amplitude of the received signal as a function of distance gives the attenuation. The signal is amplified and fed to one pair of the plates of a cathode ray oscillograph, the other pair of which is connected to the driving oscillator. Figure 19 illustrates the arrangement. The 'scope pattern provides a measure of the phase difference between the driver and the wave at any point on the sample. The smallest distance between two points in the same phase determines the wave length. Knowing the frequency of the oscillator, the velocity can be calculated. There are definite practical upper and lower limits for both the frequency and attenuation for which the method gives satisfactory results. Usually the frequency range is about 0.5–4 kc per second although Nolle mentions an upper limit of

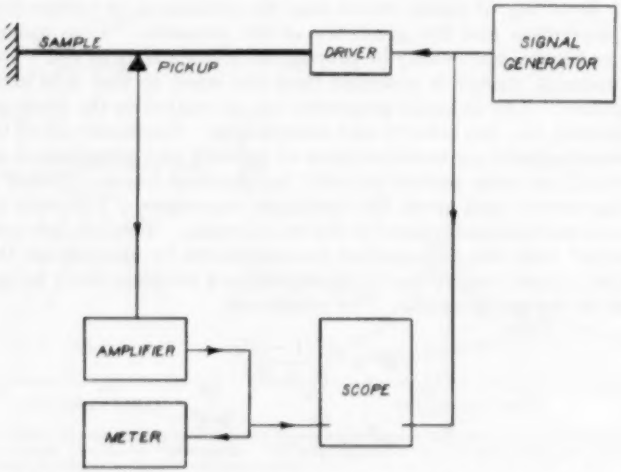


FIG. 19.—Schematic diagram of arrangements for measuring longitudinal wave propagation in rubber strips.

50 kc per second. For too low attenuations, standing waves occur and with too high attenuations, precise measurements are not possible. The strip length has been of the order of 20 or 30 cm, thickness, 0.05 cm and width 0.2 cm.

Witte, Mrowca, and Guth[47] used this method for comparing the modulus and attenuation of butyl and GR-S gum compounds over a temperature range from $-5°$ to $+90°$ C and a frequency range from 0.5 to 5 kc per second. The attenuation, as a function of temperature, showed a maximum which shifted with frequency in the way characteristic for viscoelastic measurements. The maxima for butyl rubber at the various frequencies were very broad and occurred at higher temperatures than those for GR-S. Above room temperature, the velocity and attenuation were higher for butyl than for GR-S. The trend of the velocity curves with frequency and temperature is illustrated in Figure 20 for the GR-S gum compound and the character of the attenuation curves in

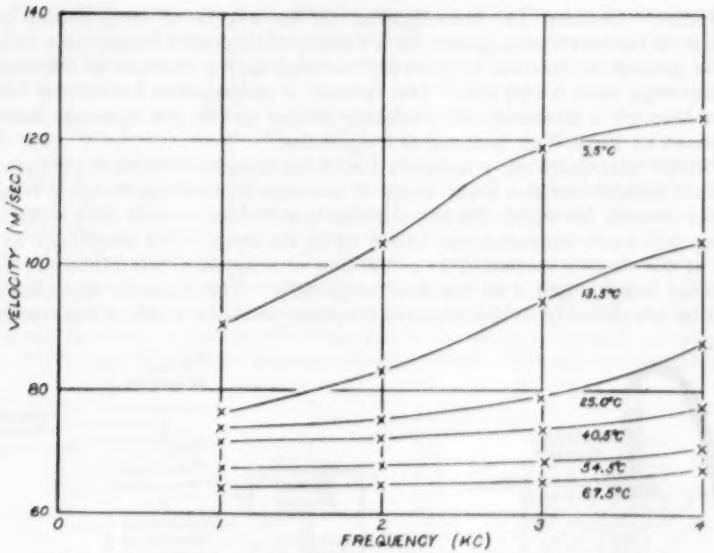


FIG. 20.—Velocity of longitudinal wave propagation for a GR-S gum compound; results of Witte, Mrowca, and Guth[47].

Figure 21. At lower frequencies, modulus vs temperature curves gave a minimum, the modulus falling at first and then rising with progressive increase in the temperature. This effect has already been discussed in connection with the work of Nolle and has been interpreted as indicating the transition from ordinary elastic to rubberlike elastic behavior.

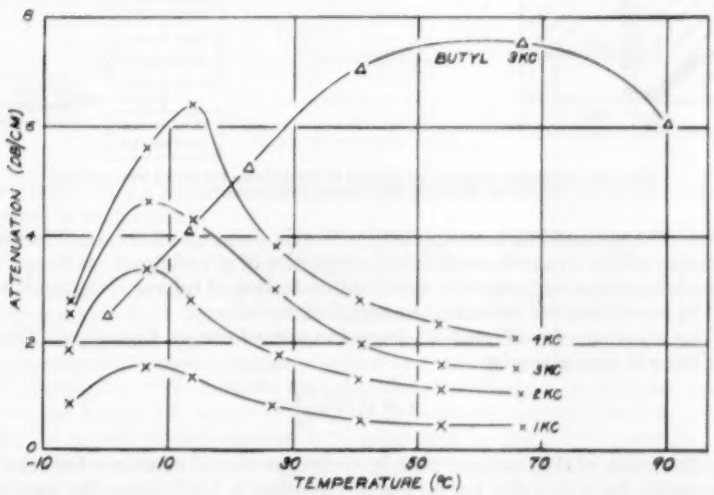


FIG. 21.—Attenuation of longitudinal waves in gum compounds; results of Witte, Mrowca, and Guth[47].

Hillier[48] included the investigation of the effects of longitudinal static strains on the wave propagation for a variety of elastomer compounds, observing in general an increase in dynamic modulus and a decrease in attenuation as the strips were drawn out. The velocity of propagation for natural rubber went through a minimum for moderate strains as did the dynamic modulus observed by Ecker[16] at mechanical frequencies.

Nolle[26] also described a modification of the longitudinal wave propagation method suitable for the lower range of acoustic frequencies, roughly below 1 kc per second, for which the attenuation is sufficiently small that a standing wave, half-wave resonance can be set up in the strip. The amplitude at one end of the strip is measured as a function of frequency, the other end being vibrated longitudinally at constant amplitude. The complex modulus may then be calculated from the resonant frequency and the width of the resonance

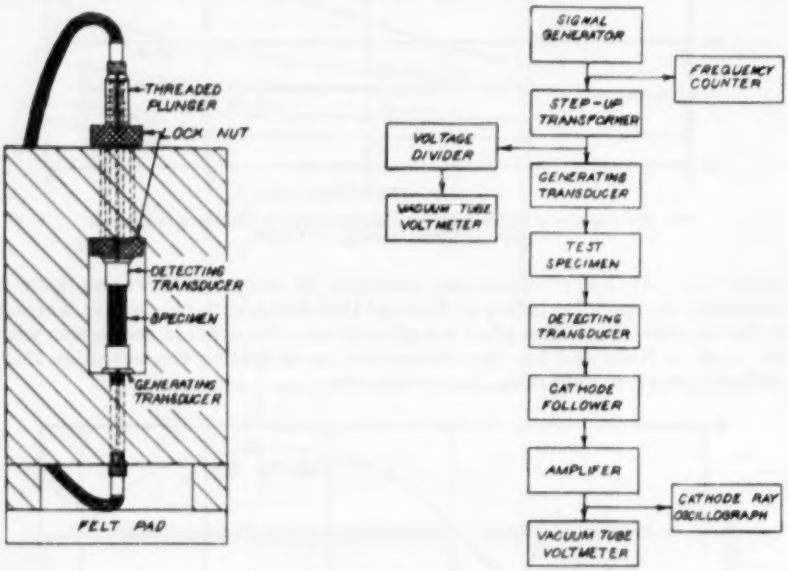


FIG. 22.—Schematic diagram for method of determining the sound transmission of rubber; Morris, James, and Guyton[49].

peak. The method has been applied by Morris, James, and Guyton[49] for measurements of the dynamic mechanical properties of a variety of elastomer vulcanizates and was suggested for specification testing of rubber compounds to be used in mountings for isolating the sound of machinery.

The equations for E' and E'' have the same form as Equations (72) and (73) but r is now given by

$$r = 0.776 \frac{\Delta f}{f_0} \tag{75}$$

Δf is the width of the resonant peak in cycles per second measured between two frequencies for which the amplitude of vibration is $1/\sqrt{2}$ times the amplitude at f_0 (compare Figure 14).

Figure 22 is a schematic diagram of the method. The test specimen was a rubber cylinder 0.75 inch in diameter and about 2.75 inches long clamped between two transducers mounted in a heavy steel frame. One transducer served as the generator and the other as the pickup. A correction was applied for the ratio of the diameter of the cylinder to the wave length of the sound. The frequency range was about 200 to 2000 cps.

A natural rubber compound at 73.5° F showed sharp resonances at 327, 638, and 903 cps corresponding to standing waves of ½, 1, and 1½ wave lengths. The multiples were not exact because the velocity increased with frequency. Butyl rubber, on the other hand, had a very flat resonance at about 900 cps due to the high internal viscosity. The sound velocity as well as E' and E''/E', tended to increase with frequency for all of the gum compounds. Natural rubber had the lowest sound velocity, lowest E' and lowest E''/E', of any of the gum compounds. Addition of carbon black increased the sound velocity, E', and E''/E', and oil addition had the opposite effect. The effect of temperature

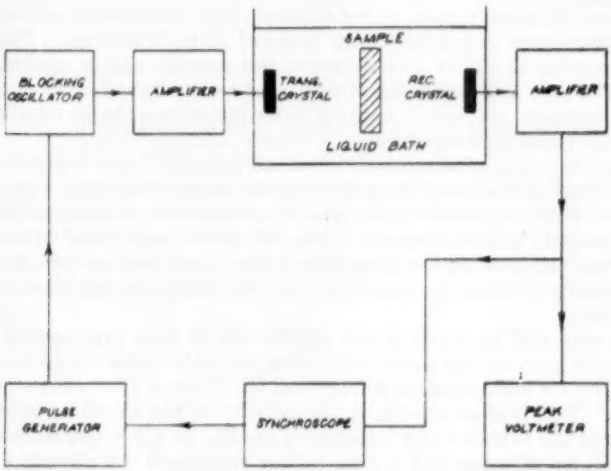


FIG. 23.—Block diagram for ultrasonic pulse propagation method; Ivey, Mrowca, and Guth[50].

was studied over a range of −10° F to +75° F. E' was found to increase with increase in temperature.

Propagation methods with pulses.—Continuous wave methods are limited on the high frequency side by the requirement that the wave length be long compared to the cross sectional dimensions of the test specimen. So pulse propagation methods have been devised which permit velocity and attenuation determinations for bulk waves and for shear waves at ultrasonic frequencies[46,50]. The electronic circuitry is rather involved and may have different modifications and refinements. To illustrate the principles, the relatively simple case may be taken, see Figure 23, where two crystal transducers are immersed in a liquid bath. A pulsed compression wave is generated by one of the crystals. The time shift and amplitude change of the signal received by the other crystal is observed when a rubber sample is inserted in the sound beam. From these values, the bulk wave velocity and attenuation can be calculated. The dura-

tion of the pulse must be short enough that interference effects do not occur between the signals but long enough that the group velocity of the pulse is essentially the same as the phase velocity of continuous waves of the same frequency. For shear waves, the sample must be in contact with one of the crystals. Cunningham and Ivey[46] used a double path technique employing two paris of crystals and two samples which varied in thickness, the rest of the sound path being through aluminum rods instead of liquid.

The interpretation of the results with bulk waves is complicated by the fact that the effective elastic modulus is a composite of the bulk modulus and shear modulus, i.e., $K + \frac{4}{3} G$. Various assumptions and approximations have been made with reasonably satisfactory results to arrive at a dynamic Young's modulus and loss factor so that the results can be used to extend curves for longitudinal wave results to higher frequencies. An alternative is to make independent measurements for shear waves as was done by Nolle and Sieck[50] and by Cunningham and Ivey[46] but the experimental procedures are by no means simple. McKinney, Edelman, and Marvin[51] have measured directly the real and imaginary parts of the dynamic bulk modulus of natural rubber-sulfur vulcanizates over a frequency range of 50 to 10,000 cps. Piezoelectric crystals serving as driver and detector, the sample, and a confining liquid were all enclosed in a cavity small compared to the wave length of the sound and the dynamic properties deduced from measurements in relation to the appropriate transducer equations.

The pulse propagation methods have had scientific interest and importance for extending the frequency range of dynamic measurements and supplying an instructive picture of viscoelastic dynamic phenomena, relaxation effects, and elastic constants in the ultrasonic region but as yet have found little technical application. In general, the character of the phenomena as regards temperature-frequency relations is consistent with the principles established at lower frequencies.

Note may well be made of the significance of bulk propagation data for rubber to be used as the cover or housing for underwater sound transducers. The velocity for bulk waves in rubber is of the order of 1500 meters per second at 20° C. This is close enough to the velocity of the sound in water so that reflection at the rubber-water interface is small. In other words, the acoustic impedance, ρc, of water and a gum rubber compound are already fairly well matched. The match can be improved, however, by suitable compounding, such as the addition of a moderate loading of carbon black. Rubber designed for this application has come to be known as rho-c rubber. The velocity of longitudinal waves in rubber, about 85 meters per second at 20° C, is of a lower order of magnitude than the velocity for bulk waves.

IV. NONLINEARITY IN DYNAMIC PROPERTIES

The early work with forced resonant vibrators[43] showed up a peculiar type of nonlinearity for the dynamic properties of rubber, especially filled compounds, in that the values for the dynamic modulus, internal friction, and resilience depend on the amplitude of vibration. However, at any one amplitude, under conditions such as shear for which the stress-strain curve is linear, the response to a sinusoidal driving force is sinusoidal without any evidence of harmonic content such as would be expected if nonlinearity is present. The nonlinearity only becomes evident when the amplitude is changed. It causes distortion of the resonance curve, see Figure 24. These effects, which have

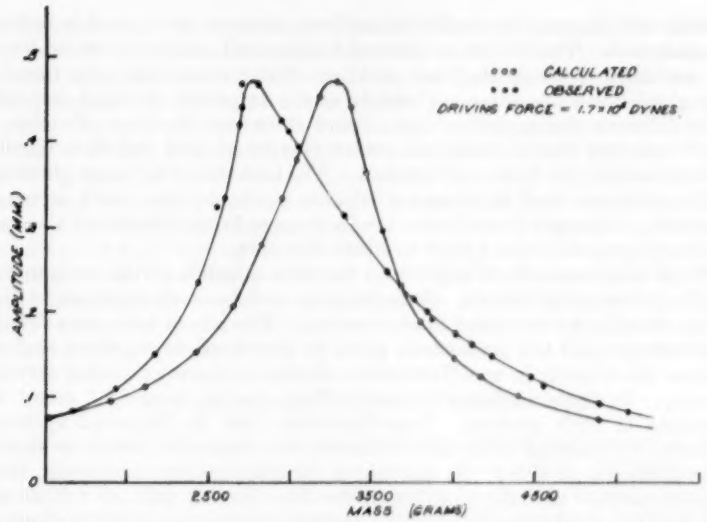


FIG. 24.—Distortion of the resonance peak for a natural rubber tread compound due to nonlinearity in the dynamic properties; Gehman, Woodford, and Stambaugh[42].

technological significance, have been rather puzzling and have been studied by Gehman, Woodford, and Stambaugh[42], Waring[27], Fletcher and Gent[43], Payne[35] and others. Curves illustrating the effect of amplitude on dynamic modulus are given in Figure 25. The tendency shown there for the dynamic modulus to

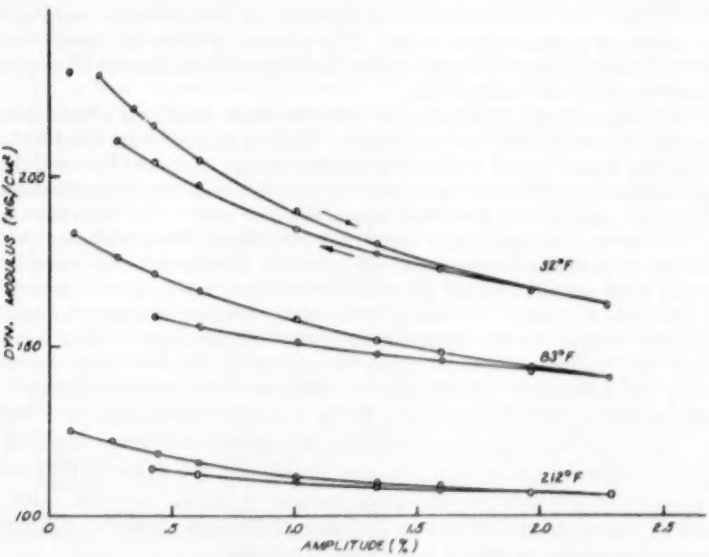


FIG. 25.—Effect of amplitude on the dynamic modulus for a GR-S tread compound; Gui, Wilkinson, and Gehman[43].

decrease with increase in amplitude has been observed under a wide variety of circumstances. The effects on internal friction and resilience are not so clear cut, probably, because they are smaller. Some observers have found the internal friction to decrease moderately as the amplitude is raised and others, under different circumstances, have found it to rise slightly. Fletcher and Gent[42] reported that it decreased rather sharply at first and then showed a gradual rise but this lacks confirmation. The best theory for these phenomena would anticipate that the internal friction would decrease with increase in amplitude. Changes in resilience due to changes in amplitude are also rather small and apparently have been in either direction.

These nonlinear effects depend on the time schedule of the measurements and the deformation history. A decrease in modulus such as shown in Figure 25 can generally be recovered upon standing. The effects have been described as thixotropic and the phenomena point to structural mechanisms analogous to those which occur in non-Newtonian colloidal systems exhibiting structural viscosity. In these nonlinear dynamic effects can be recognized many characteristics of such systems. Non-Newtonian flow in dispersed systems is attributed to the effect of the rate of shear on the orientation, shape, or structure of the dispersed particles. In the case of the filled rubber compounds, the deformable particle probably consists of the filler particle and the rubber molecules which are attached to it. The particle deformation which is dependent on the shearing stress is due to the flow characteristics of these rubber molecules attached to the filler surface. Hysteresis in retracing the nonlinear effects indicates that the temporary structural changes in filled compounds subjected to vibration probably include a breaking of molecular bonds, perhaps secondary valence bonds, which reform with a time lag. A straightening and alignment of the molecules attached to the pigment particles may also be involved, a mechanism which could be related to the temperature dependence of the nonlinear effects. For each amplitude of vibration, a different system of equilibrium molecular configurations exists. The relaxation times for these vibration produced structures are evidently rather long since the amplitude effects can be observed at quite low frequencies.

It is an interesting question as to whether these nonlinear effects actually disappear at a sufficiently low amplitude. This is generally assumed to be the case but the experimental evidence is unconvincing. Some of the modulus vs. amplitude curves of Fletcher and Gent[42] approach a constant value for the shear modulus for amplitudes less than about 0.1 per cent. On the other hand, Gui, Wilkinson, and Gehman[43] found the amplitude effect with compressive vibrations of a natural rubber tread compound to be pronounced for amplitudes less than 0.03 per cent which was the lowest value which could be measured with adequate accuracy. A closely connected question concerns the relationship of the "static" to the dynamic modulus. Apparently, in such nonlinear systems the "static" modulus cannot be reached in dynamic tests simply by reducing the frequency. In the light of what has been said, the dynamic procedure induces a different structure in the material than occurs in a "static" test. The static and dynamic moduli can be expected to become identical only when the deformations involved are comparable and the dynamic frequency is low enough for the induced structural changes to relax. Jackson, King, and Maguire[23] found large differences between static and dynamic stiffness for dynamic frequencies as low as 1 cycle in 10 minutes.

Payne[35] showed that a linear relationship existed between the log of the dynamic modulus and the amplitude and formulated equations for the effect of

filler concentration. The thinking followed lines from the variation of viscosity with shear rate of non-Newtonian solutions and the effect of filler concentration on static modulus. McCallion and Davies[25] attempted to reach a mathematical description of the nonlinear effects by employing the Superposition Principle, the elasped time function being assumed to be a fractional power of the elapsed time. Illustrative integrations for special cases were carried out, with fairly good agreement being reached for the value of the fractional exponent from relaxation and dynamic tests. In the interesting published discussion of McCallion and Davies' paper the far flung fundamental rheological implications of their approach are rather thoroughly explored and brought into relationship with the Nutting equation so well known in rheology. The trend toward bringing the nonlinear characteristics of the dynamic behavior of elastomers into the general framework of the rheology of non-Newtonian systems is becoming evident.

V. DYNAMIC AND DIELECTRIC PROPERTIES

Striking similarities in the temperature and frequency dependence of dynamic properties and dielectric properties have been recognized and studied[20,29,37,52]. The dielectric phenomena depend on the mobility for orientation of dipoles in the alternating electric field and hence are best exhibited by elastomers with polar groups such as plasticized polyvinyl chloride, copolymers of acrylonitrile, etc. Butadiene/styrene copolymers as shown by Roelig and Heideman[52] and more recently by Ecker[27] also have a maximum in the electrical loss tangent which shifts with frequency, temperature, and styrene content in a way reminiscent of the mechanical loss tangent. In both investigations, a secondary, weak maximum appeared in the curve of electrical loss tangent vs frequency. Ecker also observed secondary maxima for the dynamic damping and attributed them to a lack of homogeneity in the molecular structure of the polymer chain.

Fitzgerald and Ferry[29,52] compared the dynamic and dielectric behavior of two PVC gels over comparable ranges of audiofrequencies and temperatures and reached conclusions which no doubt have rather general applicability in regard to the relationships between dynamic and dielectric properties. The dynamic compliance, J', rather than the modulus G', is analogous to the dielectric constant so that it is advantageous in such comparisons to express the dynamic results in terms of J' and J'' rather than by G' and G''. The complex dielectric constant and mechanical compliance show the same type of frequency dispersion. The frequencies for the maxima in the electrical and mechanical loss factor curves are not the same at a given temperature, however. The electrical maximum occurred at a frequency higher by two or more powers of ten. Also, the maximum mechanical loss tangent was much greater than the maximum electrical loss tangent. But the activation energy necessary for electrical response or dipole rotation was the same as that for mechanical response hence the temperature dependence of the dynamic properties might be predicted from that of the electrical properties and vice versa. The principle of the equivalence of temperature and frequency shifts was tested with appropriate modifications and it was found that the shift factors were identical for the electrical and mechanical cases, showing that changes in dielectric constant are associated with molecular configurational changes analogous to those which affect the mechanical compliance. All of the electrical relaxation times and the mechanical retardation times appeared to have the same temperature dependence because all of the electrical data and all of the mechanical data could

be reduced to single composite curves. Nevertheless, aside from this identity in the temperature dependence, no obvious correlations were discerned between the dynamic and electrical properties other than the occurrence of a similar type of dispersion, i.e., frequency dependence.

VI. FURTHER DEVELOPMENTS FOR THE FIELD OF DYNAMIC PROPERTIES

Vibration and impact isolating, and absorbing functions are in such demand from elastomers that dynamic applications will continue to be of paramount importance. Classical examples from the automotive industry such as tires, fan belts, engine mounts, and dynamic dampers may be supplemented eventually on a large scale by rubber springing devices such as fabric-rubber air springs. Self damping springs functioning by the hydrostatic compression of an elastomer have been discussed[53]. Rubber antivibration devices are beyond the scope of this review but are typical of an active, developing field[54] for which dynamic properties are significant. Measurements of the dynamic properties of the elastomer compounds involved can usually contribute to the development of all such old and new applications, especially where precision is required in the performance. For instance, Jackson, King, and Maguire[28] estimated that at the fundamental standing wave frequency for a typical high quality rubber mounting, the transmitted force through the mounting may be about seven times as great as that expected from calculations based on low frequency data.

For scientific information on dynamic properties to be most effective, it is essential that the art of stress analysis for rubber also be developed to better characterize the complex stress distributions and cycles which are usually encountered in these practical applications. For instance, in the case of tires, the usefulness of dynamic measurements for the calculation of heat generation could be increased with improved knowledge of how the stiffness of the compounds affects the cyclic deformations in the various parts of the tire.

Laboratory work with dynamic properties for product development frequently involves a large amount of more or less routine testing for compound development. It is unfortunate that the diversity of research equipment for studying dynamic properties is so poorly represented in the testing laboratory due to the lack of standardized, well developed and commercially available instruments which would permit the various methods to be used to best advantage there. Any well equipped, general purpose rubber testing laboratory would probably have good use for at least two or three dynamic test methods. New elastomers, compounding ingredients, processing procedures, and vulcanizing systems all call for dynamic measurements for a complete evaluation and for full realization of their possibilities.

Dynamic measurements are especially significant in connection with the continuous efforts to synthesize new, improved elastomers. The essential information gained from these measurements on a very small amount of experimental polymer can be invaluable in such work. Resilience in itself is not especially characteristic of rubber. The rebound of a steel ball on a hard steel plate far surpasses any rebound which can be accomplished with rubber. Rubberlike quality for a polymer resides not merely in resilience or rebound but in the attainment of good resilience with a low dynamic modulus. Data secured by K. E. Gui with the Goodyear Vibrotester and illustrated in Figure 26 show how a plot of resilience vs dynamic modulus tends to classify gum compounds with respect to the base polymer. The points scattered along a curve for any one of the polymers were secured by varying the cure or by using differ-

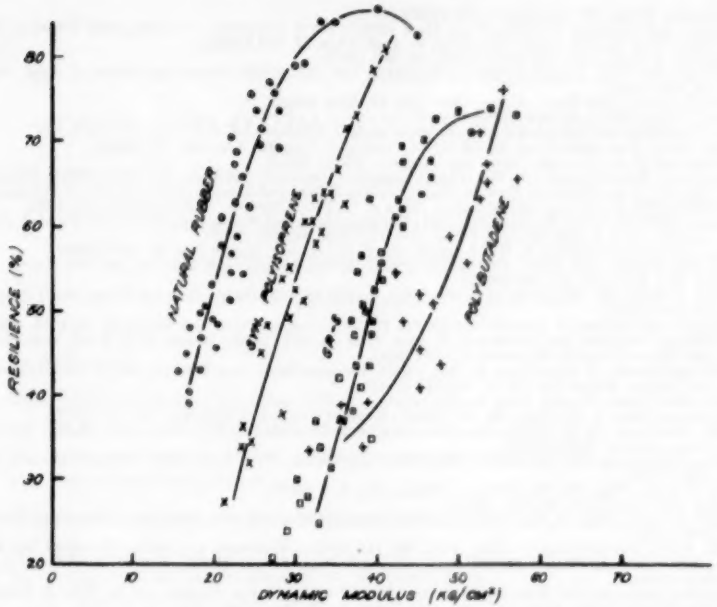


FIG. 26.—Plot of dynamic resilience vs dynamic modulus for a variety of gum compounds; unpublished work of K. E. Gui.

ent samples of polymer and thus introducing molecular weight differences and perhaps other minor structural variations. Such macromolecular features can vary the position of a point in a relatively narrow band but the micromolecular structure determines the position of this band on the resilience vs dynamic modulus plot.

Equally or even more important than these advances in the technical applications for dynamic properties are the advances to be made in the theory and fundamental understanding of the phenomena. The span of possibilities here extends beyond the limitations of a linear, descriptive theory to a complete accounting for dynamic behavior on the basis of general concepts of elastomer structure and molecular interactions.

VII. ACKNOWLEDGMENTS

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AGING AND OXIDATION OF ELASTOMERS

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I. INTRODUCTION

Natural rubber and synthetic elastomers deteriorate on aging as a result of the contribution of a number of factors. It has been generally recognized for many years[1] that the changes in properties on aging are due primarily to the deteriorating effects of one or more of the following factors: heat, light, oxygen, and ozone. Some nonoxidative thermal changes are involved but the effects of heat and light are for the most part a result of their effect upon the oxidation reaction. Thus oxygen in the form of O_2 or O_3 is the primary cause of deterioration of elastomers.

Rapid combination with ozone is a characteristic reaction of unsaturated organic compounds. In the case of rubber the reaction results in cleavage of the molecular chains with the development of surface cracks if the rubber is under stress. These cracks grow both in length and depth and soon result in serious deterioration of the material. The ozone problem is quite different from deterioration by ordinary atmospheric oxygen and is of sufficient importance to justify separate treatment in a future issue of *Rubber Reviews*. Consequently, this review will be concerned primarily with oxidative deterioration other than that due to ozone.

Both thermal and light-initiated oxidation appear to proceed by similar free-radical chain mechanisms involving the formation of hydroperoxides. Thus, information derived from one type of oxidation is usually applicable in some measure to the other. This review will be concerned primarily with thermal oxidation and the resultant effect of the oxidation upon physical properties.

Studies of the mechanism of oxidation of polymers is complicated by the difficulty of identification of both initial and final products. Small concentrations of oxygenated groups are introduced on the polymer chain and thus cannot be physically separated from the unreacted portions of the same molecular chain. It is for this reason that extensive use has been made of model compounds with similar structures in trying to determine the nature of the oxidation reaction. There is always some question as to the extent to which information obtained with simple olefins can be applied to the more complex systems of natural and synthetic rubber. Nevertheless, much of the present knowledge has been obtained in this way. In this review we will first summarize some of the pertinent information obtained with model compounds and then consider studies carried out directly on the polymers.

The problem is further complicated by the effect of various compounding ingredients as well as the effect of changes brought about by vulcanization upon the oxidation reaction and upon the resultant deterioration of properties of the vulcanized product. One question of particular interest is the way in which inhibitors or antioxidants function to reduce the rate of oxidation and retard the deterioration of properties.

This review is directed toward the factors and mechanisms involved in the aging of vulcanized elastomers as brought about by thermal oxidation of inhibited stocks. In the process it will be necessary to consider also the oxidation of model compounds and raw polymers as well as vulcanizates, and to compare inhibited and uninhibited oxidation. No attempt has been made to include all the published material on the subject since many other reviews are available[1–6]. Rather the author has attempted to interpret the present state of knowledge on aging and oxidation of elastomers, as he sees it, based on the information available at this time.

II. OXIDATION OF MODEL COMPOUNDS

Much of our present knowledge of the oxidation of elastomers and other polymeric materials is based on the more precise studies that are possible with model compounds. Bateman[7] has said: "The interaction of olefins with molecular oxygen is not only a subject of widespread industrial importance, but is one of the most thoroughly understood chemical processes." The uncertainties as to the extent to which the behavior of model compounds represents the behavior of polymers of similar structure makes us much less confident of our understanding of the chemistry of the oxidation of polymers. Furthermore, the uninhibited oxidation of pure olefins cannot be compared directly with the case of the oxidation of an unsaturated polymer in the presence of an antioxidant. Similarly the oxidation behavior of compounded and vulcanized rubber cannot be inferred directly from the oxidation of pure hydrocarbons. Nevertheless, there are certain fundamental reactions which appear to be common to all of these systems and the best place to begin is thus with the simpler cases where the nature of the products has been determined and quantitative kinetic data are available.

A. MECHANISM OF PEROXIDE FORMATION

The formation of peroxides in the oxidation of olefins was recognized in early theories, but it was not until 1939 that it was clearly established that the primary product of oxidation of simple mono-olefins was a hydroperoxide[3]. A series of studies in the laboratories of the British Rubber Producers' Research Association established the structure of the hydroperoxide in a number of cases, and kinetic studies established the free-radical chain reaction mechanism which is now generally accepted[7,8,9].

The reaction scheme may be represented as follows:

Initiation:

Production of $R\cdot$, $RO\cdot$, or $RO_2\cdot$ (From peroxide decomposition, irradiation, or other source)	r_i	R1

Propagation:

$R\cdot + O_2 \longrightarrow RO_2\cdot$	k_2	R2
$RO_2\cdot + RH \longrightarrow ROOH + R\cdot$	k_3	R3

Termination:

Bimolecular combination of radicals

$2R\cdot$	k_4	R4
$R\cdot + RO_2\cdot \longrightarrow$ Inactive products	k_5	R5
$2RO_2\cdot$	k_6	R6

The effect of oxygen concentration upon the rate of oxidation is negligible, according to this scheme, except at low oxygen pressures (less than 100 mm). At partial pressures of oxygen equivalent to air and at higher oxygen concentrations, the rate of combination of $R\cdot$ with O_2 as in R2 will be increased so that $[R\cdot] \ll [RO_2\cdot]$ and the only important termination reaction will be R6. Under these conditions, steady-state kinetics show that the overall rate of oxidation is independent of oxygen concentration.

$$\text{Rate of oxidation, } r = r_i^{\frac{1}{2}} k_3 k_6^{-\frac{1}{2}} [RH] \qquad (1)$$

At lower oxygen concentrations, the rate at which R· is converted to RO_2· by reaction R2 will be reduced and the concentration of R· radicals may become large enough relative to RO_2· so that termination by R4 and R5 becomes significant. Similarly, if the olefin is especially reactive so that reaction R3 is faster, the concentration of RO_2· will be decreased and R· increased and the rate of oxidation will be dependent upon oxygen concentration even at higher oxygen pressures. Since R3 is the only one of the propagation and termination steps with an appreciable temperature coefficient, the dependence of rate on oxygen pressure extends to higher pressures at higher temperatures[7]. Under these conditions the reaction scheme R1 through R6 gives the following relation for the rate of oxidation as a function of oxygen concentration, it being assumed that $k_5^2 = k_4k_6$ and that the kinetic chains are long[7]:

$$r = r_i^{\frac{1}{2}}k_2k_6^{-\frac{1}{2}}[RH]\frac{k_2k_6^{-\frac{1}{2}}[O_2]}{k_3k_4^{-\frac{1}{2}}[RH] + k_2k_6^{-\frac{1}{2}}[O_2]} \qquad (2)$$

When reaction R2 is sufficiently faster than R3 so that $[R\cdot] \ll [RO_2\cdot]$, as noted previously, the more general Equation (2) simplifies to give Equation (1). Thus when sufficient oxygen is available the maximum rate given by Equation (1) is attained. When the oxygen pressure is reduced to a sufficiently low value (dependent upon temperature and the relative reactivity of the olefin) the rate of oxidation is limited by the availability of oxygen.

The dependence of rate of oxidation upon oxygen concentration at low concentrations, and the lack of dependence at higher concentrations was demonstrated experimentally[8] in the case of the oxidation of ethyl linoleate under mild conditions (45° C). This reduction in rate of oxidation at low oxygen concentration with simple olefins is not to be confused with the dependence of rate of inhibited oxidation of vulcanized rubber on oxygen concentration at both low and high oxygen pressures[10], as will be discussed later.

The nature of the termination reaction R6 has been the subject of recent studies. Russell[11] has demonstrated a kinetic isotope effect in the termination step with secondary peroxy radicals in the oxidation of ethylbenzene and various deuterated derivatives at 60° C with initiation by α,α'-azodi-*iso*-butyronitrile (AIBN). The α-phenethylperoxy radicals interacted 1.9 times faster than the α-deutero derivative indicating that a C—H bond is broken in the termination step:

$$2RO_2\cdot \longrightarrow \text{Stable products} + O_2$$

The per cent oxygen found as hydroperoxide varied with the kinetic chain length and the relative amounts of peroxide and acetophenone formed are consistent with the reaction:

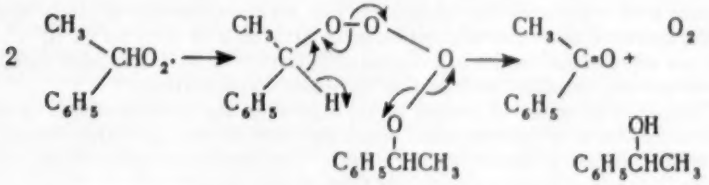
$$2C_6H_5CHCH_2O_2\cdot \longrightarrow C_6H_5COCH_3 + C_6H_5CHOHCH_3 + O_2$$

A tertiary peroxy radical derived from cumene could give no kinetic isotope effect and the yield of hydroperoxide in that case was essentially quantitative and independent of the kinetic chain length (number of times the propagation cycle repeats before termination). The reaction in this case has been formulated to provide for hydroperoxide formation in the termination step also:

$$2C_6H_5C(CH_3)_2O_2\cdot \longrightarrow C_6H_5C(CH_3)_2OOH + C_6H_5CCH_3{=}CH_2 + O_2$$

The proposed mechanism of termination in the case of primary and secondary peroxy radicals is considered to involve a cyclic transition state or unstable

intermediate which undergoes homolytic cleavage to give the observed products:



B. PEROXIDE DECOMPOSITION AND AUTOCATALYTIC BEHAVIOR

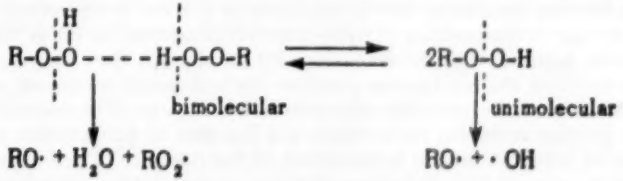
The rate of oxidation of simple olefins at ordinary temperatures increases regularly with the extent of oxidation and the overall rate is found to be proportional to the first power of the hydroperoxide concentration. Since Equation (1) shows the rate to be a function of the square root of the rate of initiation, it follows that the only important initiation process under these conditions is a bimolecular peroxide decomposition:

$$2ROOH \longrightarrow RO\cdot + RO_2\cdot + H_2O \qquad k_1 \qquad R1$$

$$\text{Rate of initiation, } r_i = k_1[ROOH]^2 \qquad (3)$$

Careful studies of the early stages of oxidation under mild conditions reveal a departure from linearity in the early stages of the plot of rate vs. oxygen absorbed[7]. The observed behavior corresponded to an initial dependence on the square root of the hydroperoxide concentration at low peroxide concentrations, indicating initiation by a first-order decomposition of peroxide which is superseded by a second-order decomposition at higher concentrations of hydroperoxide.

Changes in the infrared spectrum of a pure hydroperoxide on dilution[12] show that the hydroperoxide is associated by hydrogen bonding in the pure form and that dilution gives a progressive dissociation. Thus at higher peroxide concentration the hydrogen bonded dimer apparently undergoes a bimolecular decomposition while at low peroxide concentration, or under conditions favoring dissociation of the dimer, a unimolecular decomposition is observed:



Higher temperatures favor dissociation of the hydrogen bonded dimer, and the kinetic effect of the unimolecular decomposition persists to higher concentrations of peroxide at higher temperatures[7]. This interpretation of the kinetics of hydroperoxide decomposition explains many of the earlier inconsistencies in the literature in regard to the experimentally observed order of the reaction. The bimolecular decomposition is observed only with hydroperoxides since peroxides of the type ROOR would be incapable of association by hydrogen bonding and consequently only unimolecular decomposition would be observed.

Initiation by direct oxygen attack on the olefin either at the double bond or on the *alpha* methylene group is also possible, and probably occurs in the initial reaction with a peroxide-free olefin. It has not been possible to study this reaction, however, since the absorption of as little as 0.02–0.05 ml O_2 (0° C, 760 mm) per ml of olefin results in a degree of initiation by hydroperoxide sufficient to obscure any possible contribution by direct oxygen attack[12].

The catalytic effect of certain metal ions upon the decomposition of olefin hydroperoxides is of interest since small amounts of iron and other metals are frequently present as impurities in rubber. The primary reaction in the case of ferrous iron and a hydroperoxide has been shown to be[13]:

$$Fe^{++} + ROOH \longrightarrow RO\cdot + Fe^{+++} + OH^-$$

This reaction is typical for a metal ion capable of being oxidized to a higher valence state by a one-electron transfer. Subsequent steps vary with the nature of the metal and the peroxide. Cobalt ions serve to decompose hydroperoxides in both valence states so that a chain reaction results in which the sum of the two steps gives the same products as in bimolecular thermal decomposition (R1).

$$ROOH + Co^{++} \xrightarrow{\text{rapid}} RO\cdot + OH^- + Co^{+++}$$

$$ROOH + Co^{+++} \xrightarrow{\text{slow}} RO_2\cdot + H^+ + Co^{++}$$

$$2\ ROOH \xrightarrow[\text{ions}]{\text{cobalt}} RO\cdot + RO_2\cdot + H_2O$$

The effect of metal ion catalysis is thus to increase the rate of initiation by peroxide decomposition. Since the propagation reaction R3 produces another hydroperoxide, the rate of the catalyzed initiation will continue to increase until the rate of peroxide formation and decomposition are balanced and a steady state is attained. The kinetic chain length will decrease as the rate of initiation increases and will approach unity as the overall rate of oxidation approaches its limiting value[7].

Any factor which promotes initiation by peroxide decomposition will lead to a similar situation in which the rate of formation and decomposition of hydroperoxide become equal. Thus Tobolsky, Metz, and Mesrobian[14] observed that higher temperatures, presence of activators, and light activation all lead to a limiting maximum rate of oxidation at a given temperature. Using the bimolecular decomposition of hydroperoxide illustrated in R1 as the initiation reaction, together with the other steps R2 through R6, they show by steady-state kinetics that the mechanism predicts (for sufficiently advanced stages of autoxidation) that the peroxide concentration and rate of oxidation will approach a limiting mximum value which is a function of temperature and concentration of substrate and is independent of the presence of activator. This prediction is supported by experimental evidence that light accelerates the rate of oxidation of vulcanized rubbers until at each temperature a critical light intensity is reached beyond which a further increase in light intensity has no effect. At higher temperatures where the thermal oxidation has already attained the maximum rate, addition of light does not accelerate the rate of oxidation.

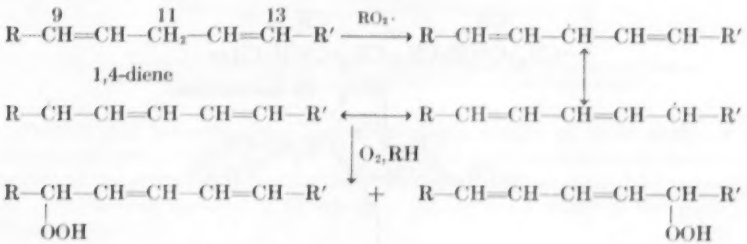
These authors[14] note that various complications may modify the predictions of the theory in specific actual cases. For example, a side reaction causing destruction of the hydroperoxide (without the production of chain-initiating radicals) would also bring about the phenomenon of steady states of hydroper-

oxide concentration. Actually, in the case of simple olefins, the peroxide concentration usually goes through a maximum and then decreases[15] rather than to maintain a constant limiting value as predicted by theory. Thus the theory is only applicable to the autocatalytic stage of the reaction where complicating side reactions are of lesser importance.

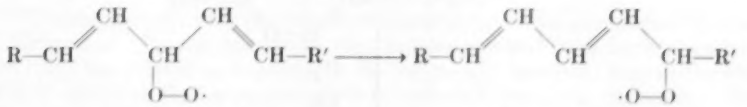
The maximum constant rate of oxidation observed by Tobolsky and coworkers[14] in the autocatalytic stage of oxidation of vulcanized rubber is essentially an uninhibited oxidation since any inhibitors present initially have become ineffective at that advanced stage of oxidation. Their limiting maximum rate is thus not to be confused with the constant-rate stage in the oxidation of inhibited rubber vulcanizates which is observed prior to the start of the autocatalytic stage[10,16].

C. PRODUCTS OF OXIDATION

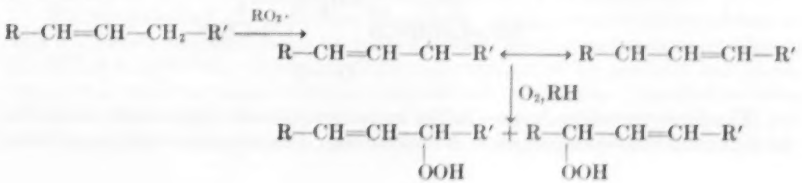
The primary products of oxidation of unsaturated hydrocarbons are peroxides. Mono-olefins and 1,4-dienes give mainly α-hydroperoxides by the mechanism already described. The 1,4-dienes such as the esters of linoleic acid are much more reactive than mono-olefins since the reactive methylene is alpha with respect to two double bonds. The product appears to consist mainly of conjugated peroxides as a result of oxidative isomerization of the double bond[7] rather than the nonconjugated product corresponding to the original structure. The pentadienyl radical may be represented by three resonance forms so that reaction of the radical with O_2 could take place at either positions 9, 11, or 13 in the linoleate chain:



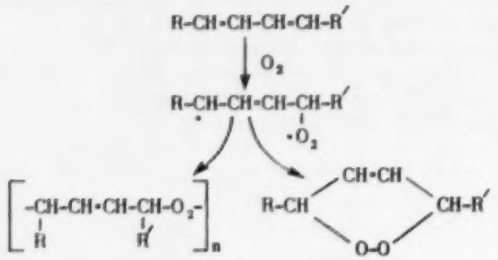
Apparently reaction at positions 9 and 13 is favored, or if reaction does occur at position 11 also, the nonconjugated peroxy-radical readily rearranges to a thermodynamically favored conjugated form:



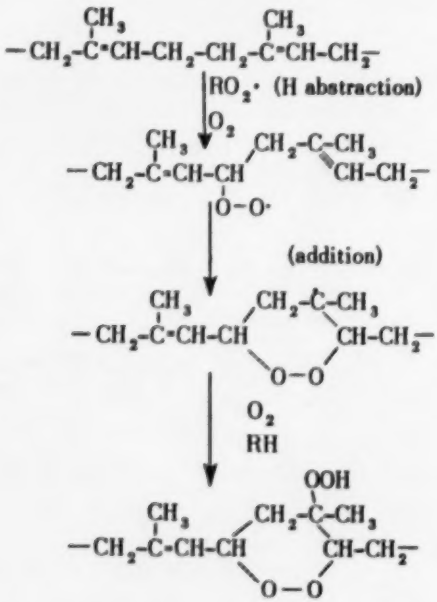
Allylic isomerization also occurs with mono-olefins to give isomeric hydroperoxides:



Conjugated (1, 3) diolefins react with oxygen by 1,4-addition rather than hydrogen abstraction. The biradical formed may give either polymeric peroxides or cyclic peroxides[8]:



The model compounds for natural rubber and synthetic rubbers derived from conjugated dienes are the 1,5-dienes. For example, the low molecular weight polyisoprenes have been studied extensively in this connection[3]. These 1,5-diolefins exhibit both types of reactivity with peroxy radicals. They react by hydrogen abstraction like mono-olefins and 1,4-dienes to form an α-peroxy radical which adds to an adjacent double bond by a reaction analogous to the behavior of conjugated dienes and olefins with terminal unsaturation. The resulting product appears to be a cyclic diperoxide[8] formed by a multistep process which merely adds two steps to the propagation cycle:



The hydroperoxides formed in the initial reaction of oxygen with olefins fail to explain oxidative degradation of elastomers. Chain-scission and crosslinking

reactions are considered to be the major cause of drastic changes in properties of polymers and vulcanizates which take place during aging in the presence of oxygen. These reactions are apparently either side reactions or subsequent reactions resulting from peroxide decomposition. Oxidative studies of model compounds have yielded such complex products that the mechanism of the degradation processes has not yet been established. Considerable information is available, however, as to some of the products of peroxide decomposition[2,13], but relatively little precise information has been reported for secondary alkyl hydroperoxides of the type expected to form in the oxidation of natural and synthetic elastomers.

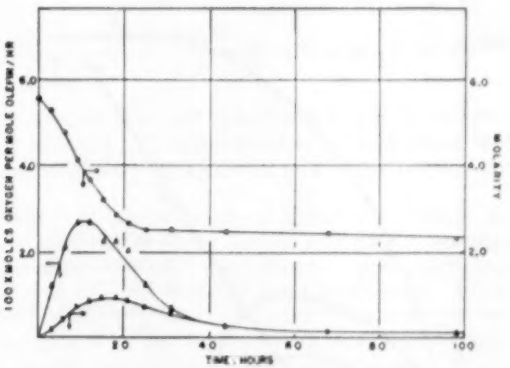


FIG. 1.—Variation of rate and olefin and peroxide contents with time for oxidation of 5-phenyl-2-pentene at 90° C. ○, unreacted olefin; ×, peroxide; △, rate.

Farmer and his coworkers[17] interpreted the results of their study of the oxidation of cyclohexene at 40° C as evidence for the formation of alcohol and epoxide as the primary products of thermal decomposition of the hydroperoxide. The peroxide was considered to oxidize a double bond either in the same or a different molecule.

Ketones are one of the important products of oxidation as reported by many investigators. Farmer considered that ketones resulted from further reactions involving the alcohol and epoxide. He recognized, however, that in the presence of catalysts, the hydroperoxide is dehydrated directly to carbonyl. Most subsequent authors have indicated the formation of ketones directly from the hydroperoxide. This is reasonable since acids which are also formed as products of subsequent reactions could readily catalyze such a decomposition.

We have studied the oxidation of a series of phenyl-substituted olefins in this laboratory as model compounds for a butadiene-styrene synthetic rubber of the GR-S type[15,18–20]. Hydroperoxide was determined by analysis but no attempt was made to isolate the hydroperoxides in pure form. Qualitative tests for aldehyde showed them to be present in the early stages of oxidation but not after prolonged exposure to oxygen at 100° C. In the case of 1-phenyl-2-bu-

tene, benzoic acid and phenyl 1-propenyl ketone were isolated from the oxidation mixture and identified[18]. The most likely source of the ketone in this case would be from the corresponding hydroperoxide formed by oxidation on the methylene *alpha* to both the double bond and the phenyl group.

The oxidation of 5-phenyl-2-pentene was studied at both 80° and 100° C[20]. Oxygen uptake was followed quantitatively and changes in the concentrations of unreacted olefin, peroxide, carbonyl, ester, carbon dioxide, and water were determined at successive time intervals. Acids present in the final oxidation mixture, both free and combined as esters, were identified by chromatographic analysis.

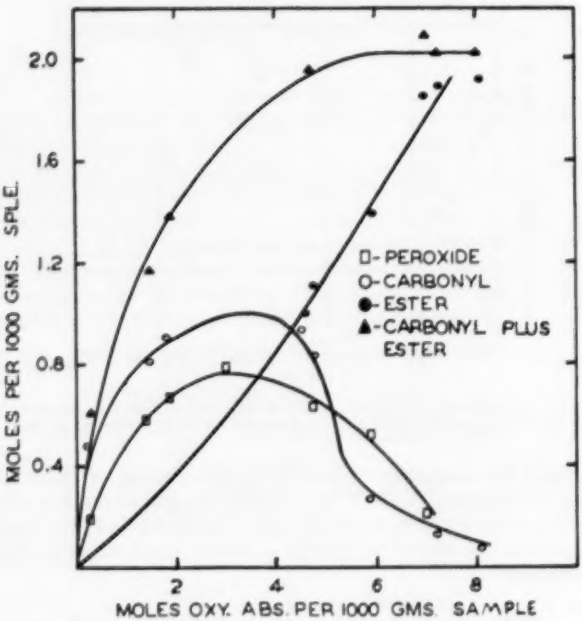
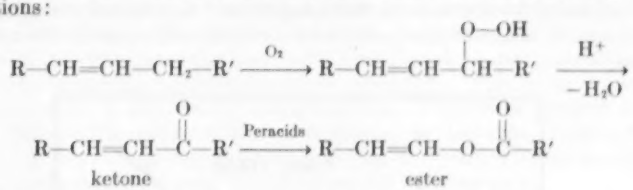


FIG. 2.—Concentration of peroxide, carbonyl, and ester as a function of oxygen absorbed in oxidation of 5-phenyl-2-pentene at 80° C.

Figure 1 illustrates a typical case in which the concentration of olefin and peroxide are compared with the observed rate of oxidation at various times[19]. The rate is approximately proportional to the product of the concentrations of peroxide and unreacted olefin consistent with the mechanism of Bolland as expressed in Equation (1). Both rate and peroxide concentration go through a maximum rather than maintain a steady state as predicted by the theory of maximum rates[14]. The decreasing phase indicates the effect of side reactions which consume peroxide without the production of chain-initiating radicals.

Changes in peroxide, carbonyl, and ester concentrations with oxygen absorption at 80° C are compared in Figure 2. The similarity of the peroxide and carbonyl curves suggests that ketone is formed directly from hydroperoxide. The decrease in carbonyl concentration accompanied by a simultaneous increase in ester concentration suggests that ketone is being converted to ester. The

curve for ester plus carbonyl levels off at a fairly constant maximum value in the region where ester continues to increase while carbonyl decreases. It is known[21] that ketones can be oxidized directly to esters by peracids, and since peracids are probably present in the reaction mixture as the first product of oxidation of aldehyde intermediates, it is reasonable that esters may be formed primarily from ketones under these conditions rather than by esterification of alcohols with acids. These results are consistent with the following sequence of reactions:



Analyses for epoxide were not conclusive due to interference of carbonyl and ester in the analysis. It appeared that a small amount of epoxide was present and reaction of these groups with acid would provide another route to ester formation.

The acids formed in the oxidation of 5-phenyl-2-pentene, as identified by chromatographic analysis, included formic and acetic (found only as ester) together with benzoic, crotonic, phenylacetic, and phenylpropionic acids. Phenylpropionic was the acid found in greatest amount. It could be formed by direct oxygen attack at the double bond of 5-phenyl-2-pentene as well as by alpha methylenic attack on the 5-phenyl-1-pentene isomer which was shown to be present in the starting material by infrared analysis. Infrared absorption studies on oxidized samples indicated the presence of carbonyl, epoxide, and hydroperoxide as well as both internal and terminal unsaturation.

The loss of unsaturation was nearly linear with oxygen absorbed. Much of this decrease is probably due to polymerization induced by oxy radicals rather than to direct saturation with oxygen since most of the oxygen absorbed was accounted for in the oxygenated products: peroxide, carbonyl, ester, acid, carbon dioxide and water.

Studies of the oxidation of model compounds have obviously contributed much to our knowledge of the products of oxidation and the fundamental mechanism of the oxidation reaction. However these studies tell us relatively little about the nature of the chain-scission and crosslinking reactions which are primarily responsible for the degradation of properties of elastomers. Consequently, we must go to oxidation and aging studies on polymeric materials in order to study these reactions and to see the extent to which information obtained with the model compounds is applicable to the elastomers they represent.

III. OXYGEN-ABSORPTION STUDIES ON ELASTOMERS

A. INTRODUCTION

Quantitative measurements of the amount of oxygen absorbed by rubber polymers and vulcanizates have been particularly useful in fundamental studies of oxidation and aging. Many variations of apparatus and experimental methods are described in the literature[2,22,23]. Dufraisse[1] and his coworkers used a manometric apparatus and have been credited[2] with popularizing the oxygen-absorption method. The volumetric method used in our own labora-

tory[10,16,24,25] was adapted from the method of Kohman[26]. The most recent version of our equipment was constructed by starting with a commercially available aluminum heating block of the type used for aging in individual test tubes. The necessary gas burettes, leveling bulbs, sample tubes, etc., were added to give a 14-tube volumetric oxygen-absorption apparatus similar to the apparatus described in a previous publication[25].

Lump calcium oxide is placed in the sample tubes to react with carbon dioxide and water formed as oxidation progresses. A constant average pressure is maintained by manual adjustment with a precise setting at the time readings are taken.

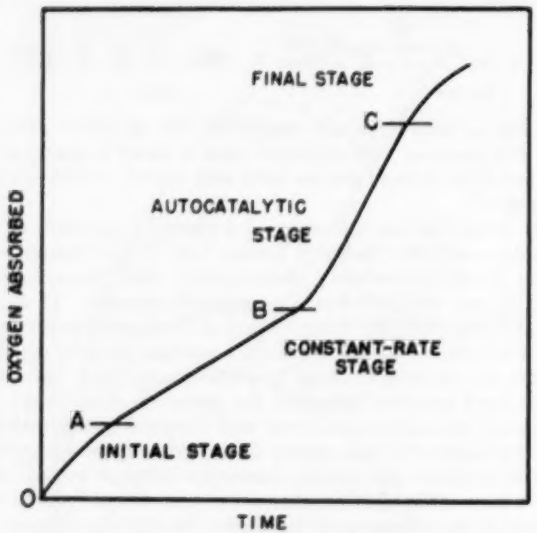


FIG. 3.—Four stages observed in oxygen-absorption measurements on elastomers.

The curve for oxygen absorption vs time in Figure 3 illustrates a hypothetical case in which all four stages of the reaction are present. In actual practice one seldom observes the complete curve in a given case, either because one or more stages are not present, or because the experiment is terminated before the later stages are reached. The initial stage, OA, is usually quite evident in the thermal oxidation of vulcanizates. It is more pronounced in black stocks than in gum stocks[27], and is frequently absent in the case of the uncompounded polymer[28]. This stage is not present in the oxidation of pure olefins[15].

The amount of oxygen absorbed in the initial stage is relatively small as compared to the total curve but it is nevertheless significant. Greater changes are frequently observed in modulus and tensile strength for a given amount of oxygen absorbed in this stage than in any other. Some of these changes are probably the result of thermal effects such as after vulcanization which are superimposed upon the oxidative effects so that both are reflected in the observed changes in physical properties. The initial stage is sensitive to changes in procedure and is more difficult to reproduce than the constant-rate stage which follows. Nevertheless, some rapid oxygen-absorption test methods are

based on rates obtained in this first stage[29] and the results are generally qualitatively in agreement with measurements extending into the later stages of oxidation.

The constant-rate stage (AB in Figure 3) is quite reproducible in thermal oxidation of inhibited elastomers and their vulcanizates[16]. This stage appears to be controlled by the antioxidant and the duration of the stage varies with antioxidant concentration[30]. It is analogous to an induction period in the oxidation of olefins except that it is a stage of retarded oxidation rather than complete inhibition. Kinetic studies based on variations in the constant-rate stage with oxygen concentration have contributed to our knowledge of the mechanism of oxidation and antioxidant action[10,21]. This stage, together with the initial stage, is particularly important from a practical point of view since the combined OAB portion of the curve represents the range of useful life of the rubber. When the autocatalytic stage begins, the properties are soon degraded to a point where the material is unsatisfactory for most uses.

The autocatalytic stage (BC in Figure 3) corresponds to the autooxidation of simple olefins. Uninhibited polymers and vulcanizates behave quite similarly in that the first two stages are frequently either absent or too small to be detected[20]. It is in this stage that Tobolsky, Metz, and Mesrobian[14] observed a limiting maximum rate of oxidation consistent with the theoretical prediction based on the mechanism of oxidation developed by Bolland and coworkers[8] with model compounds.

The changes in rate as oxidation progresses are evident from examination of Figure 3. The rapid initial rate levels off to a constant rate which persists for some time if sufficient inhibitor is present. The rate then increases autocatalytically and may again attain a constant rate as it goes through a limiting maximum value and then drops to a very low rate in the fourth and final stage which probably continues for a very long time. This final stage may represent depletion of oxidizable groups, a limitation of rate of diffusion by an oxidized surface layer, or in some cases, the formation of oxidation products which act as auto-inhibitors. The oxidation of certain sulfur compounds has been shown to produce a comparable stage of auto-inhibition[32].

B. SOME FACTORS IN THE OXIDATION OF ELASTOMERS

1. *Effect of cure.*—The nature and state of cure has considerable effect upon the oxidation of vulcanizates. This is particularly evident with natural rubber where the rate of oxidation increases with cure[26] probably as a result of the thermal inactivation of natural antioxidants. This effect goes through a maximum so that in one example[24] after the first 20 minutes at 280° F additional time of cure gave a small but consistent decrease in rate of oxidation. Butadiene-styrene rubber is less sensitive to variation in time of cure than natural rubber[16]. The effect of minor variations in time of cure is much smaller in the case of oxygen-absorption measurements than in the case of aging as measured by changes in physical properties of the vulcanizate. In order to minimize the effect of cure in oxygen-absorption work, a time of cure should be selected which is somewhat beyond the usual optimum based on tensile strength and modulus values. This will ensure that any variations will be in the region where additional time of cure has only a very small effect upon rate of oxidation.

2. *Effect of surface area.*—The possible limitation of rate of oxidation by the rate of diffusion of oxygen into the sample must be recognized and avoided by proper choice of sample thickness. The simplest way to do this is to employ

a range of sample thicknesses and observe the limiting value beyond which a further reduction in thickness gives no increase in rate of oxidation. A series of studies in this laboratory[25] has established safe limits of sample thickness for a number of typical gum and black vulcanizates including natural rubber and four synthetic types. The values change with temperature so that thinner samples are required at higher temperatures. Raw polymers and gum vulcanizates require thinner samples at a given temperature than vulcanizates containing carbon black. The value also varies with the rate of oxidation so that an uninhibited material needs to be thinner than an inhibited sample. For the same reason a thickness which is satisfactory for kinetic studies in the constant-rate stage may be quite unsatisfactory for quantitative rate studies in the autocatalytic stage. These published values should be useful in helping

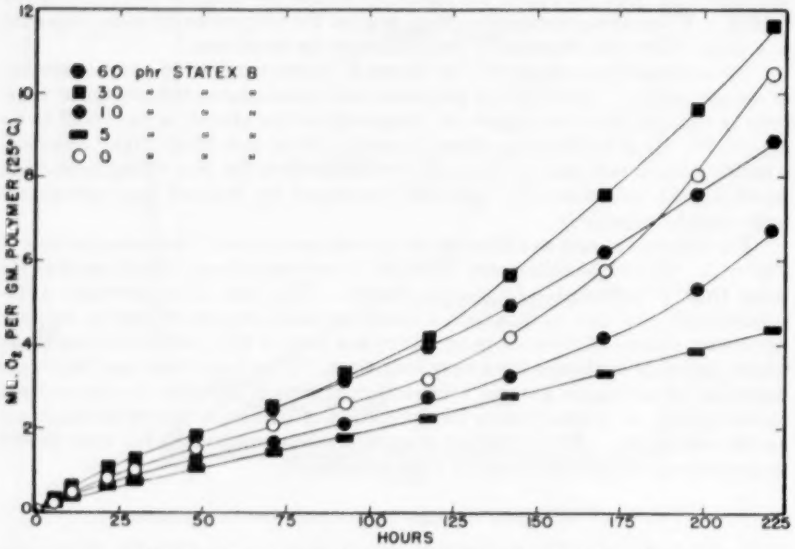


FIG. 4.—Effect of carbon black content on oxidation of uninhibited peroxamine GR-S 1500 vulcanizate at 70° C.

to select suitable thicknesses for conventional aging studies as well as for oxidation. Buist has included a table of sample thicknesses (reproduced from the paper cited above) for this purpose in his recent monograph[2] on aging and weathering of rubber. It should be emphasized that these values were established for the constant-rate stage and that deviations from the formulations, temperatures, and oxygen concentration employed may alter the situation.

3. *Effect of carbon black.*—The effect of carbon black upon the oxidation of elastomers is of particular importance due to the common use of reinforcing carbon blacks in many commercial applications including tires. An accelerating effect of carbon blacks on the rate of oxygen absorption was demonstrated some years ago with GR-S vulcanizates and the additional oxygen absorbed was shown to be reflected in a greater modulus increase on aging[27]. Kuzminskii[33] and coworkers proposed that the accelerating effect was due to adsorption of antioxidant on the carbon surface in a form that made it unavailable as an in-

hibitor. This has been disproved by a recent study with uninhibited elastomers which showed that the accelerating effect was observed even in the absence of antioxidant[34].

An inhibiting effect of carbon black on the oxidation of cold rubber polymer and certain vulcanizates has been reported in a series of papers by Sweitzer and coworkers[35]. Both an inhibiting effect at low carbon loadings and an accelerating effect at higher loadings has been observed in the case of one cold rubber vulcanizate[34] as illustrated in Figure 4.

The effect of carbon black upon the oxidation and aging behavior of elastomers is clearly quite complex and involves a number of competing effects. The accelerating effect may be attributed to a number of factors including a direct catalytic effect upon the oxidation reaction and a catalysis of peroxide decomposition to free radicals. Adsorption of antioxidant may be involved to some extent but this alone cannot account for the observed behavior. The increased

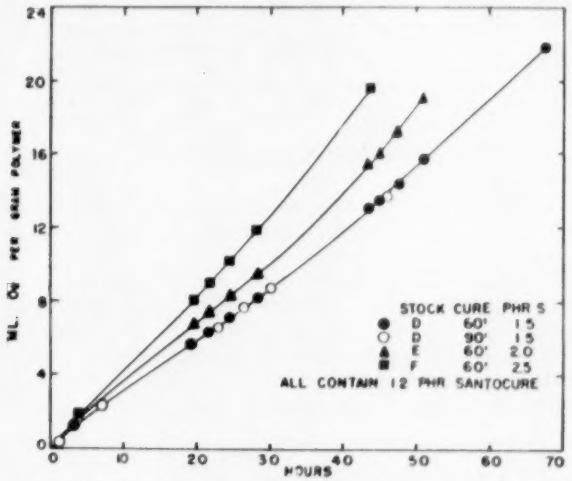


FIG. 5.—Effect of sulfur variation on oxygen absorption of GR-S black stock at 110° C.

solubility of oxygen when carbon black is present in the rubber may also contribute to the increased rate of oxidation, as suggested by van Amerongen[36], although this effect decreases at higher temperatures. The inhibiting effect may also be attributed to several factors including the activity of the carbon surface as a free-radical acceptor[37], interaction of the carbon with iron and certain other metal ions with a mutual reduction in the normal catalytic effect of both[34], and the effect of carbon black upon the decomposition of peroxides to stable products in the presence of certain types of inhibitors[31] as will be discussed later. Thus the observed behavior in any given case will depend upon the relative contribution of these individual ways in which carbon black appears to be capable of functioning to alter the oxidation reaction.

4. *Effect of sulfur.*—The effect of sulfur upon oxidation and aging of elastomers is of particular importance since heating with sulfur and accelerator is the most widely used method of vulcanization. It is generally recognized that low-sulfur stocks exhibit better resistance to aging than high-sulfur stocks.

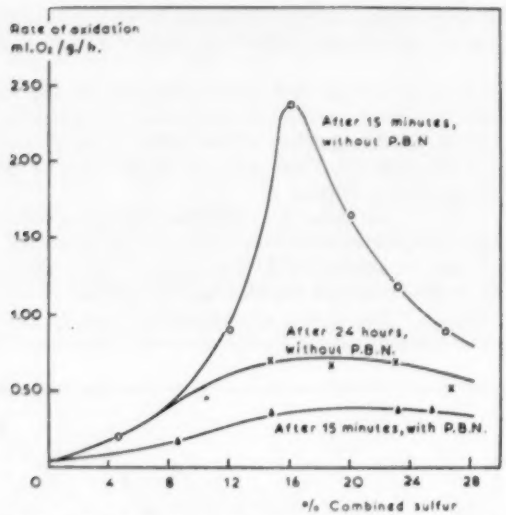


FIG. 6.—Effect of combined sulfur on rate of oxidation of vulcanized natural rubber at 80° C.

Work at the rubber laboratory of the Rock Island Arsenal indicates that non-free-sulfur curing systems give better aging resistance than conventional sulfur-accelerator cures[38].

Oxygen-absorption studies show that the rate of oxidation of both natural and synthetic rubber vulcanizates increases with the amount of sulfur used in the cure[39]. Figure 5 illustrates the case for a series of GR-S black stocks exposed to oxygen at 110° C. It should be noted that additional time of cure for the low-sulfur stock did not affect the rate. The increased absorption of oxygen produced a correspondingly greater change in properties.

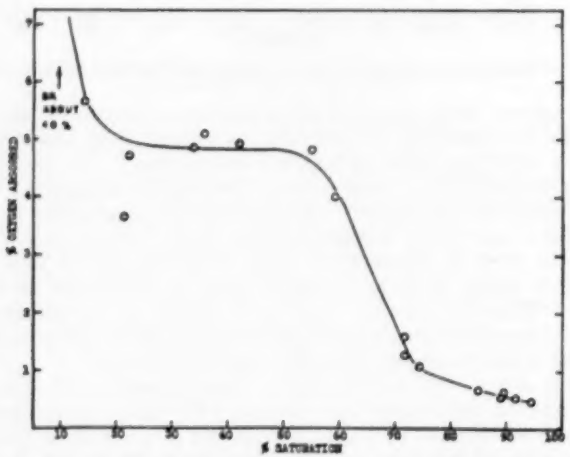
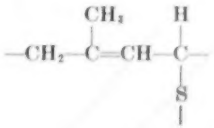


FIG. 7.—Oxygen absorbed after 140 hours vs percent saturation of CH_3SH-PB elastomers.

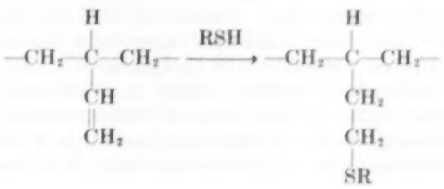
The effect of combined sulfur upon rate of oxidation was shown by van Amerongen[40] to go through a maximum at about 16 per cent combined sulfur as illustrated in Figure 6. The decreasing rate at higher concentrations was attributed to two factors: (1) the slow diffusion of gases in the ebonitelike products, and (2) a decrease in the active oxidizable places in the rubber.

The increased rate of oxidation with higher levels of combined sulfur up to the maximum rate appears to be associated with an activation of the adjacent C—H group rather than to a direct oxidative attack on the sulfur linkage. This activating effect of sulfur is particularly evident when adjacent unsaturation is also present. Work in this laboratory[41] on saturated and unsaturated sulfur compounds showed that *tert*-butyl disulfide did not react with oxygen at a measurable rate at 100° C, while *n*-butyl sulfide reacted slowly and allyl sulfide reacted rapidly under the same conditions. Structures such as the following in which a hydrogen is on a carbon *alpha* to both the sulfur and a double bond could account for the observed behavior:



A series of studies by Bateman and coworkers[32] on the oxidation of organic sulfides showed that saturated sulfides are relatively inert to thermal oxidation while allylic sulfides are more reactive initially than comparable unsaturated hydrocarbons. Sulfoxides are formed by reaction of peroxides with sulfides but not by direct attack of O_2 on the sulfide link. The unsaturated sulfides showed evidence of autoinhibition by products of oxidation in that the curves leveled off at relatively small oxygen uptakes.

Further evidence that the increased rate of oxidation observed at higher sulfur levels is a result of the combined effect of sulfur and unsaturation rather than to the sulfur link as such is provided by the superior aging properties of saturated rubbers containing sulfur. For example, adducts of mercaptans with elastomers, in which most of the double bonds have been saturated, have recently been shown to absorb oxygen at a very low rate as compared to the original unsaturated polymers[42]. Figure 7 shows that oxygen absorption at 100° C decreased with increasing amounts of sulfide sulfur introduced into polybutadiene by addition of methyl mercaptan with a corresponding reduction in unsaturation. The large decrease in oxidizability with the first 20 per cent of saturation was attributed to the observed more rapid saturation of side-chain vinyl groups as compared to internal double bonds. This would remove the activating effect of the unsaturation on the reactive tertiary hydrogen atoms at the point of branching. An isopropyl mercaptan adduct was even more selective in saturation of the vinylic groups and imparted a correspondingly greater resistance to oxidation.



The effect of the remaining unsaturation in a partially saturated adduct of mercaptan and rubber may be to provide a site for initiation of oxidation. Radicals formed in this way could than attack a C—H link adjacent to a sulfide link. This could account for the level portion of the curve in Figure 7 since the effect of introducing more sulfide links would tend to make up for the decreasing amount of unsaturation. The essentially saturated adduct then becomes unreactive in the absence of autoxidizing unsaturated hydrocarbon as was demonstrated with model compounds[32].

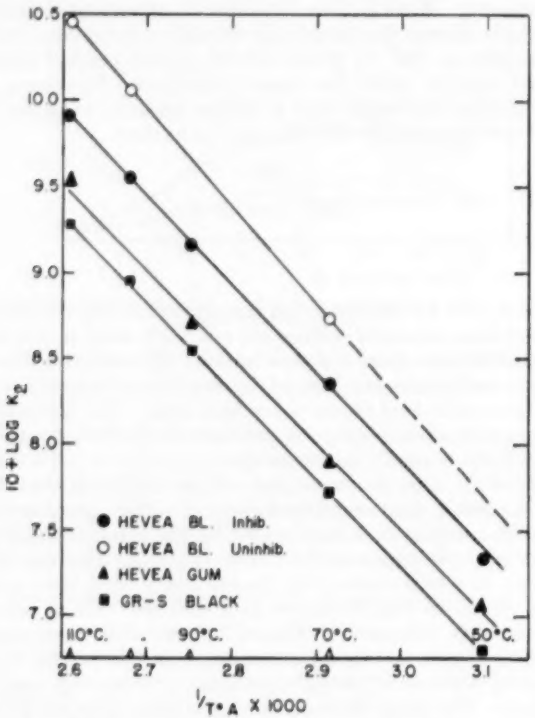


FIG. 8.—Effect of temperature upon rate of oxygen absorption of vulcanizates.

5. *Effect of temperature.*—The accelerating effect of temperature upon oxidation and aging is well known[1,42]. Quantitative studies show that the effect of temperature on the rate of oxidation in the constant-rate stage is regular and reproducible[41]. Figure 8 is an Arrhenius-type plot of rate vs the reciprocal of the absolute temperature. These data indicate that the same mechanism extends over the entire range of temperatures studied, with an overall activation energy in the range of 24 to 26 kcal per mole. The additional oxygen absorbed at the higher temperatures causes more extensive deterioration of physical properties. However, the ratio of chain scission to crosslinking is changed, scission being favored at higher temperatures, while crosslinking is of greater relative importance at lower temperatures. Thus the aging character-

istics of a stock cannot be deduced from an accelerated test at a single temperature, but if the trend is established by tests at more than one temperature, it is possible to extrapolate to other temperatures and predict both the rate of oxygen uptake and the probable effect upon physical properties[44].

6. *Effect of oxygen concentration.*—The effect of oxygen concentration is also important in any attempt to correlate the results of accelerated tests in oxygen with the predicted behavior on aging in air. The rate of oxidation of unsaturated hydrocarbons is independent of oxygen concentration above a small minimum value in the absence of inhibitors, but the rate of inhibited oxidation in the constant-rate stage has been found to be a function of the square root of the oxygen concentration[10,45]. Typical data are shown in Figure 9. The theoretical significance of this relationship is discussed later under mechanism of

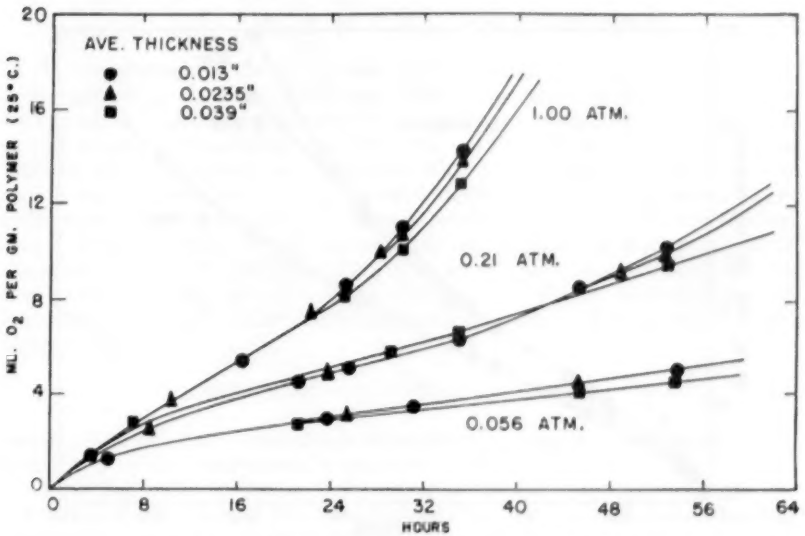


FIG. 9.—Oxygen absorption of inhibited Hevea black stock at 100° C and various partial pressures of oxygen.

inhibited oxidation. Deterioration of properties increases with the oxygen concentration, as would be expected, but the ratio of chain scission to crosslinking also changes. Scission is favored at higher oxygen concentration while crosslinking appears to be of greater relative importance during aging at lower oxygen concentrations.

Accelerated aging tests frequently involve both an increase in temperature and oxygen concentration. Both of these changes increase the rate of oxygen uptake and also increase the proportion of chain scission for a given amount of oxygen absorbed[46]. Thus aging at high temperatures and high oxygen concentrations will result in increased decay of tensile strength. Since this is the most evident sign of deterioration of natural rubber, it follows that a natural rubber vulcanizate will stand up better in air at normal temperatures than predicted by the accelerated tests. In the case of butadiene-styrene rubbers, the opposite will be true since oxidative hardening is the most serious aspect of aging

in this case and this will reflect the higher proportion of crosslinking for a given amount of oxygen absorbed at the lower temperature in air.

C. INHIBITED OXIDATION AND ANTIOXIDANT ACTION

1. *Evaluation of antioxidants.*—Oxygen-absorption methods have proved to be quite useful for evaluation of antioxidants[20]. In most cases, the change in physical properties is in proportion to the oxygen absorbed, but there are some exceptions in which the degradation reactions are altered without a corresponding change in the rate of oxidation[47,48]. Consequently, it is desirable to supplement comparative oxygen-absorption measurements with data on changes in physical properties with aging. Most antioxidants exhibit an optimum concentration at which the rate of oxidation in the constant-rate stage is at a mini-

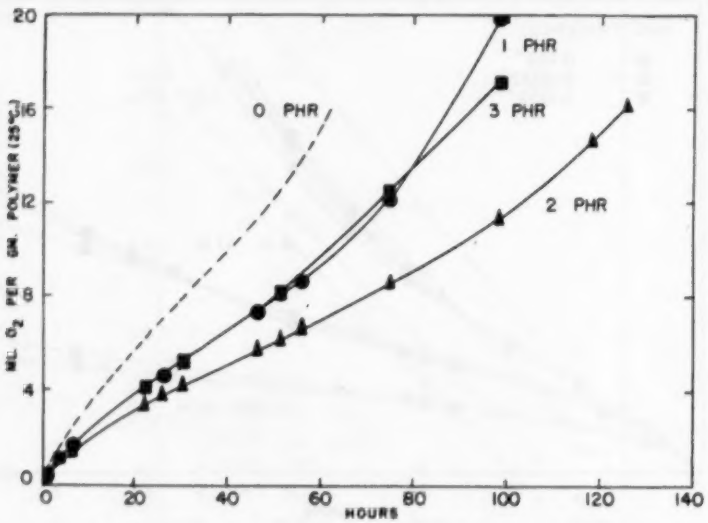


FIG. 10.—Oxygen absorption of Hevea black stocks containing various concentrations of phenyl-2-naphthylamine, 90° C.

mum. Either more or less antioxidant results in more rapid oxidation[21,48] relative to this minimum value. A typical example is shown in Figure 10 for phenyl-2-naphthylamine in a natural rubber tread-type stock containing 50 parts of an EPC carbon black. In some cases higher concentrations of antioxidant may give even higher rates of oxidation than the uninhibited control, but even in such a case the inhibited stocks retain their properties on aging better than the uninhibited material. Relative to the optimum concentration, however, the additional oxygen absorbed at the higher antioxidant concentrations is usually harmful as shown by a correspondingly increased deterioration of properties in the majority of the cases studied[48].

2. *Mechanism of inhibited oxidation.*—The constant-rate stage in volumetric oxygen-absorption measurements appears to be controlled by the antioxidant, both from the standpoint of rate of oxidation and the duration of the stage. Consequently, rate studies involving this stage are particularly useful for in-

vestigation of the mechanism of inhibited oxidation and antioxidant action. The effect of oxygen concentration on the rate is particularly significant in this connection. The example in Figure 9 illustrates a case in which the rate in the constant-rate stage was found to be directly proprtional to the square root of the oxygen concentration. In other cases a somewhat more complex equation was required. Three different relationships have been observed experimentally[10,21] as illustrated by the following empirical equations for the effect of oxygen concentration on the rate, K_2, of inhibited oxidation (in the constant-rate stage):

$$\text{Rate, } K_2 = kP^{\frac{1}{2}} \qquad \text{(strongly inhibited)} \qquad (4)$$

$$K_2 = k(P + a)^{\frac{1}{2}} \qquad \text{(weakly inhibited)} \qquad (5)$$

$$K_2 = k(P + a)^{\frac{1}{2}} + \gamma P \qquad \text{(different accelerator)} \qquad (6)$$

The dependence of the rate of inhibited oxidation on oxygen concentration is in contrast to the uninhibited autocatalytic oxidation of pure unsaturated hydrocarbons which is independent of oxygen concentration except at very low oxygen pressures (usually less than 100 mm). If the same propagation reactions (R2 and R3) are involved, any differences must come in the initiation or termination steps. Since none of the plausible termination mechanisms would require oxygen, it follows that the oxygen dependence must involve the initiation step. From Equation (1) it is seen that the rate of oxidation is proportional to the square root of the initiation rate so that an initiation reaction involving the first power of the oxygen concentration would be consistent with the observed behavior, provided the termination remains bimolecular. A termination mechanism of the type

$$RO_2\cdot + AH \longrightarrow RO_2H + A\cdot \text{ (stable)} \qquad R4$$

results in a prediction of first power dependence on oxygen concentration which is contrary to the experimentally observed behavior[10].

A mechanism of oxidation and antioxidant action consistent with the observed kinetics is obtained with the addition of two initiation reactions involving direct oxygen attack on hydrocarbon and on antioxidant, a chain transfer cycle, and bimolecular termination reactions involving the antioxidant. There is also evidence (as will be shown later) that certain antioxidants reduce initiation by peroxide decomposition, and to account for this a reaction is also postulated in which the antioxidant destroys the peroxide by promoting decomposition to stable products rather than to chain-initiating free radicals[21]. The following mechanism in which the antioxidant has a possible fourfold action is consistent with the observed behavior:

Initiation

(Peroxide decomposition)	$xROOH \xrightarrow{k_1} nR\cdot (RO\cdot, RO_2\cdot)$	R1
(Direct O_2 attack on hydrocarbon)	$RH + O_2 \xrightarrow{k'_1} R\cdot$	R1′
(Direct O_2 attack on antioxidant)	$AH + O_2 \xrightarrow{k''_1} A\cdot$	R1″

Propagation		
	$R\cdot + O_2 \xrightarrow{k_2} RO_2\cdot$	R2
	$RO_2\cdot + RH \xrightarrow{k_3} RO_2H + R\cdot$	R3
Chain transfer		
(With antioxidant)	$RO_2\cdot + AH \xrightarrow{k'_4} RO_2H + A\cdot$	R4′
	$A\cdot + RH \xrightarrow{k'_5} AH + R\cdot$	R5′
Termination		
	$2RO_2\cdot \xrightarrow{k_6}$ stable products	R6
(Chain stopping by antioxidant radical)	$2A\cdot \xrightarrow{k'_6}$ stable products	R6′
	$A\cdot + RO_2\cdot \xrightarrow{k''_6}$ stable products	R6″
Peroxide destruction		
(Antioxidant-induced decomposition)	$ROOH \xrightarrow[AH]{k_a}$ stable products	R7

The four ways in which an antioxidant might act would then be:

1. Initiation of oxidation chains by direct oxygen attack on the antioxidant.
2. Chain transfer involving the antioxidant, but without termination.
3. Termination in which an antioxidant radical reacts with another radical to give stable products and thus end the oxidation chain.
4. Direction of peroxide decomposition to stable products, rather than to free radicals which could initiate further oxidation.

A theoretical equation has been derived[21] from this mechanism by steady-state kinetics to give the following expression for the rate, K_2, in the constant-rate stage:

$$K_2 = b(P + cK_2)^{\frac{1}{2}} + a(P + dK_2) \tag{7}$$

Solving equation (7) for K_2, the equation can be converted[21] to the form:

$$K_2 = a(1 + \sqrt{1 + \beta P}) + \gamma P \tag{8}$$

The last terms in Equation (7) and (8) are both first power with respect to oxygen pressure and clearly correspond to the γP term in the empirical Equation (6). If γ is small, the term can be neglected giving Equation (5). The oxygen pressure term, P, represents the contribution of initiation by direct oxygen attack while the term "a" in Equation (5) corresponds to the term cK_2 in the theoretical Equation (7) and represents the contribution of initiation by a process independent of oxygen concentration, presumably by peroxide decomposition. Indeed the value of "a" in Equation (5) varied with the rate so that much better agreement with the experimental data was obtained when cK_2 was used to replace it. Thus the theoretically derived equations based on the proposed mechanism for inhibited oxidation are of the same form as the empirical equations which describe the observed behavior.

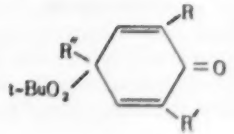
It appears then that the value of "c" represents the contribution of peroxide

decomposition to the initiation process and that the ratio $cK_2/(P + cK_2)$ is a measure of the proportion of initiation by peroxide decomposition. The accompanying table[31] shows how these values vary with antioxidant concentration and with a change from black stocks to a gum stock:

			$\frac{cK_2}{P+cK_2}$	
Hevea black stocks, 90° C		c	O_2	Air
Uninhibited		7.2	0.60	0.73
PBNA	1 phr	2.8	0.27	0.46
	2	0	0	0
	3	0	0	0
Santoflex B	1	0	0	0
Hydroquinone	1	4.1	0.38	0.54
Deenax	3	35.7	0.78	0.81
Antioxidant 2246	3	10.2	0.64	0.77
Hevea gum stocks, 100° C				
PBNA	2 phr	4.4	0.38	0.63
Snatoflex B	1	7.1	0.49	0.73
Deenax	3	8.0	0.47	0.73
Antioxidant 2246	3	17.1	0.57	0.79

The reduction in the value of "c" effectively to zero with higher concentrations of phenyl-2-naphthylamine (PBNA) explains why a simple square root dependence on oxygen concentration was observed with strongly inhibited stocks Equation (4) while weakly inhibited stocks required the more complex Equation (5). It is also apparent that phenolic antioxidants are not as effective in this particular connection as the amines, but that it is only in the presence of carbon black that the amines differ from the phenols in this regard. It is on the basis of these data that it was postulated that amine antioxidants are capable of decomposing hydroperoxides in the presence of carbon blacks to give stable products as indicated in R7 and thus reduce the contribution of peroxide decomposition to the initiation process. A possible mechanism for this type of peroxide decomposition will be discussed in the following section along with evidences from other studies.

3. *Mechanism of antioxidant action.*—The mechanism of antioxidant action has been the subject of many studies, and while it is not yet clearly established, considerable progress has been made. In the reaction scheme presented for inhibited oxidation we have assumed a hydrogen abstraction mechanism, which is followed either by a chain transfer reaction or a chain stopping mechanism involving a bimolecular combination of radicals. This scheme is consistent with the results obtained by Bickel and Kooyman[49] in their extensive studies of antioxidant action. They carried out competitive reactions of $RO_2\cdot$ with antioxidant, AH, and hydrocarbon, RH, and measured initial rates of oxidation. The results with phenolic antioxidants were consistent with a hydrogen abstraction mechanism, with termination either by combination of two $A\cdot$ radicals or $A\cdot + RO_2\cdot$ as in R6′ and R6″. Chain transfer was shown to be consistent with an optimum antioxidant concentration at which the rate is at a minimum even as observed experimentally. Product studies showed the formation of compounds of the type:



Two radicals are thus used up per molecule of phenol present, one by hydrogen abstraction and the other by addition to the ring. The stoichiometry of $2RO_2\cdot$ per molecule of inhibitor was also found by Hammond and coworkers[50] in a majority of cases studied and similar products were isolated.

Kuzminskiĭ and Angert[51] correlated antioxidant efficiency with structure in arylamines and reached the conclusion that groups which change the strength of the N—H bond alter the effectiveness of the antioxidants. Groups which increased the mobility of the labile hydrogen increased the antioxidant efficiency.

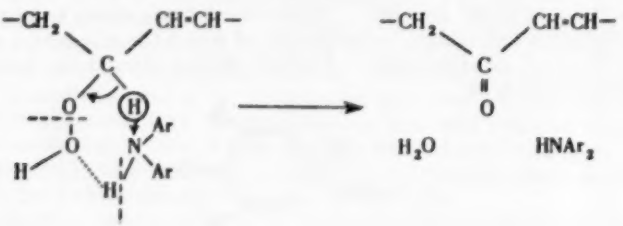
The situation with amine antioxidants is more complex than with phenols and alternate mechanisms have been proposed as discussed later. In Bickel and Kooyman's recent study[49] of amine antioxidants they were unable to isolate the reaction products of $RO_2\cdot$ with amine antioxidants, but the observed kinetics were of the same type as previously observed with phenols, and were likewise consistent with a hydrogen abstraction mechanism.

It is possible that different types of antioxidants may function by different mechanisms and even a given antioxidant may function in more than one way. The observed kinetics and products which are consistent with initial abstraction of hydrogen can also be accounted for by addition of $RO_2\cdot$ to the aromatic ring with subsequent loss of hydrogen. The known antioxidant activity of tertiary amines requires another explanation and the most plausible one is electron abstraction[52] to form an ion radical (like that of a Würster cation) and the ultimate formation of stable products.

$$RO_2\cdot + Ar\ddot{N}R_2 \longrightarrow RO_2{:}^{\ominus} + Ar\dot{N}R_2{}^{\oplus}$$

Some materials which exhibit an inhibiting effect on oxidation may function as deactivators for metal impurities which would otherwise catalyze the oxidation.

Kennerly and Patterson[53], in studies of petroleum antioxidants, have called attention to a group of compounds which they call peroxide decomposers. These materials destroy peroxides, presumably by a polar mechanism, to give stable products and thus prevent peroxide initiation. Phenols, mercaptans, and sulfonic acids are included which could function by an acid catalysis analogous to the decomposition of cumene hydroperoxide to form phenol and acetone. Aliphatic sulfides have some activity but the outstanding example in their work was a zinc dialkyl dithiophosphate. The mechanism in these cases is not clear. This type of activity is analogous to the activity of amine antioxidants which, in the presence of carbon black, appear to reduce peroxide initiation. A plausible mechanism for destruction of peroxide by an amine antioxidant may be represented by an initial association through hydrogen bonding which results in a dehydration of the hydroperoxide by a polar mechanism as illustrated by the following structures:



Thus we have evidences for at least five ways in which antioxidants may function:

1. Hydrogen donation to $RO_2\cdot$ to form RO_2H
2. Electron donation to $RO_2\cdot$ to form $RO_2:^{\ominus}$
3. Addition of $RO_2\cdot$ to the aromatic ring (either directly or through a π-complex) with subsequent loss of hydrogen.
4. Deactivation of metal impurities which would otherwise catalyze the oxidation.
5. Destruction of peroxide (probably by a polar mechanism) to give non-radical products.

Individual substances may function in any one of these ways or they may exhibit various combinations of these several ways in which antioxidants appear to be capable of acting to reduce the rate of oxidation. In addition, certain antioxidants may also act as promotors of thermal oxidation by direct oxygen attack on the antioxidant and also participate in a chain transfer mechanism as already discussed. The catalytic effect of certain antioxidants in photo-oxidation is also well known[54].

D. KINETIC ISOTOPE EFFECT IN INHIBITED OXIDATION

The mechanism of antioxidant action most often assumed to account for the effectiveness of secondary aryl amines and phenols involves the removal of a labile hydrogen by a peroxy radical as the initial and controlling step of the reaction. This mechanism is supported both by kinetic studies and by isolation of subsequent reaction products in some cases[49].

$$ArOH + RO_2\cdot \longrightarrow ArO\cdot + RO_2H$$
$$Ar_2NH + RO_2\cdot \longrightarrow Ar_2N\cdot + RO_2H$$

If this assumption is correct, it is reasonable to expect that substitution of a labile hydrogen by deuterium should give rise to a kinetic isotope effect. The rate of chain termination should be slower with deuterium than with hydrogen and thus the rate of oxidation of the substrate should be increased by the substitution. Support for this expectation is found in a study of the reaction of acyl peroxides with phenols in which O—H was replaced by O—D. Several peroxide-phenol-solvent systems showed a small but constant isotope effect, indicating that O—H cleavage is a rate-controlling step in that reaction[55]. An isotope effect involving cleavage of a C—H bond has been observed in the uninhibited autoxidation of a deuterated olefin[56].

Two studies are reported in the literature in which the investigators were unable to demonstrate an isotope effect in oxidation systems employing amine antioxidants. Hammond, Boozer, and coworkers[50] studied the oxidation of cumene and tetralin in chlorobenzene in the presence of diphenylamine and methylaniline and reported no significant difference in the rate of oxidation when deuterium replaced hydrogen in the amine. Pedersen[52] found no difference in the induction period of gasoline oxidation when deuterium replaced the amino hydrogen in N,N′-diphenyl-*p*-phenylenediamine. On the basis of their failure to observe an isotope effect, together with arguments against a mechanism in which $RO_2\cdot$ adds as a first step at a specific position on the aromatic ring, Hammond and coworkers[50] postulate the formation of a π-complex between

$RO_2\cdot$ and the aromatic ring as a first and reversible step. Pedersen[52] proposed electron donation by the antioxidant as the preferred mechanism for amines while still proposing hydrogen donation as the characteristic mechanism with phenolic inhibitors.

A recent note from Bickel and Kooyman[57] challenges the conclusions of Hammond and others that the absence of an observable isotope effect precludes the primary abstraction of hydrogen as the mechanism for the action of amine and phenolic antioxidants. They point out that a low activation energy would result in a small isotope effect. Data on the autoxidation of 9,10-dihydroanthracene initiated by 2,2,3,3-tetraphenylbutane and retarded by a hindered phenol are presented. It is deduced from the effect of temperature on the re-

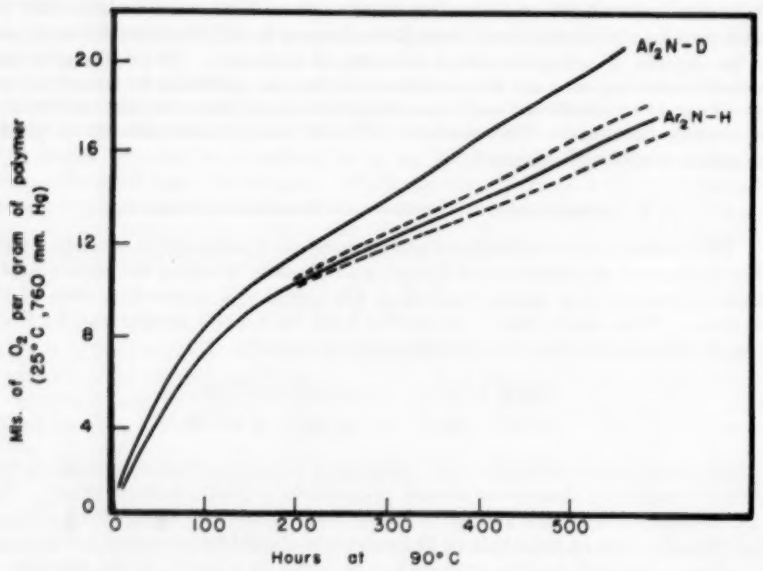


FIG. 11.—Kinetic isotope effect in the oxidation of butadiene-styrene polymer inhibited with 3 phr of normal and deuterated N-phenyl-2-naphthylamine, 90° C, 1 m. O_2at.

action that the energy of activation for the step in which $RO_2\cdot$ reacts with AH is close to zero in that case. They also report an isotope effect of $k_H/k_D = 1.95$ for the reaction of a less reactive radical, diphenylpicrylhydrazyl with a hindered phenol at 20° C and 30° C. The activation energy in this case was 5.3 kcal/mole. They admit that the difference between the radical studied and an alkylperoxy radical is such that it does not prove that $RO_2\cdot$ radicals also react at the phenolic OH group.

Recent studies in this laboratory[58] have demonstrated a kinetic isotope effect in the inhibited oxidation of a butadiene-styrene polymer with both amine and phenyl antioxidants. The results obtained with normal and deuterated N-phenyl-2-naphthylamine at 3 phr concentration are shown in Figure 11. The dashed lines show the calculated standard deviation of the data and the curve for the deuterated antioxidant falls well outside the limits of the curve

for the normal antioxidant. The ratio k_D/k_H was 1.8 ± 0.3 for the rate of oxidation in the constant-rate portions of the curves as obtained at 90° C in oxygen with a deuterium substitution of not less than 60 per cent. The isotope effect was not detectable when only 1 phr of inhibitor was used. A similar study involving 2,6-di-*tert*-butyl-*p*-cresol at 3 phr concentration gave a ratio of k_D/k_H of 1.3 with not less than 77 per cent deuterium substitution. It is interesting that this is the same value reported by Walling and coworkers[55] for the k_H/k_D ratio in the reaction of acyl peroxides with phenols.

The demonstration of an isotope effect in the inhibited oxidation of an elastomer as reported above tends to reestablish the hydrogen abstraction mechanism as a rate-controlling step in the case of these well-known antioxidants of the diaryl amine and hindered phenol types. It must be recognized however that other competing mechanisms may also be involved even in these cases, and that with other types of antioxidants alternate mechanisms may predominate. All five of the mechanisms listed in the preceeding section are supported by observed behavior in individual cases.

IV. DEGRADATION OF PROPERTIES

Oxygen has been recognized as a prime factor in the deterioration of elastomers from very early studies of aging of natural rubber[1,2]. In the early days of synthetic rubber some questions were raised as to whether this was also true for a butadiene-styrene copolymer, but it was soon established that oxygen is likewise a major factor in the aging of synthetic elastomers[49]. One recent paper[38] has sought to minimize the importance of oxygen as compared to the nature of the curing system. The point which they ignore in this comparison is that the nature of the curing system affects the susceptibility of the vulcanizate to oxidation, and thus the observed importance of choice of curing system is in part a result of the effect upon oxidative degradation. Nevertheless, it must be recognized that nonoxidative degradation also occurs. Consequently, we will briefly review some of the factors other than oxygen which have been shown to cause deterioration, before we discuss the relation of oxygen absorption to changes in physical properties.

A. NONOXIDATIVE DEGRADATION OF ELASTOMERS

1. *Thermal degradation.*—Oxidative and nonoxidative thermal degradation of rubber have been compared by van Amerongen[40]. Heating natural rubber and GR-S in the absence of oxygen produced little deterioration of properties at moderate temperatures, for example, up to 100° C. At higher temperatures, for example, 150° to 250° C, purely thermal degradation produced changes in properties comparable to those produced by oxygen at temperatures 60° to 100° C lower. Thus a rubber that resists aging in air at 100° may be unstable when heated to 180° even in the absence of oxygen.

The superior aging resistance of natural rubber vulcanized with tetramethylthiuram disulfide without the addition of free sulfur is attributed to a low rate of reaction with oxygen which in turn may be attributed to a very low content of combined sulfur. This superiority does not extend to thermal degradation, however[40]. Considerable devulcanization or reversion of the gum stock was observed on heating in the absence of oxygen at temperatures of 150° and higher, and the black stock showed more deterioration of tensile strength than a comparable stock vulcanized with sulfur and accelerator.

Accelerated aging studies thus reflect the combined effect of oxidative and thermal degradation. Changes due to a continuation of the vulcanization process on heating may also be superimposed upon the degradation reaction in the early stages of aging of many vulcanizates.

2. *Mechanical rupture of chains.*—Watson and coworkers[60] have demonstrated and explained the scission of molecular chains as a result of cold mastication of elastomers. When the change in Mooney viscosity after mastication is plotted against the temperature of mastication in air, a minimum breakdown is observed at a temperature just above 100° C. At higher temperatures the greater decrease in viscosity is attributed to oxidative scission, but at lower temperatures the greater breakdown is attributed to a mechanical rupture of primary bonds to form free radicals as a result of the greater shearing forces in cold mastication. The role of oxygen in cold mastication is to combine with the R· radicals to form RO_2· and thus prevent the recombination of two R· radicals which would offset the effect of the original rupture. Little breakdown is observed during cold mastication in an inert atmosphere unless substances capable of combining with radicals are added. It is suggested that the mode of action of many peptizers for softening synthetic rubber during mastication is by this mechanism rather than by their functioning as oxidation catalysts.

Chemical verification of the mechanism has been obtained by the use of spectroscopic and tracer techniques to measure the incorporation of the radical acceptors into the polymer. Further verification of radical formation by cold mastication is found in the formation of interpolymers when a vinyl monomer is present in the rubber being masticated[61].

Further evidence of mechanical scission is found in the interaction of rubber and carbon black during milling to form an insoluble carbon black-gel complex. It has been proposed that the carbon black functions as an electron donor in this reaction and combines with the R· radicals to form covalent bonds[62].

The observed rate of scission on cold mastication, as reflected in viscosity and molecular weight changes, is not consistent with a random cutting of molecules. Rather, the data are found to be consistent with a preferential breaking of the longer chains so that the observed breakdown tends to level off at a limiting value of molecular weight and viscosity[61,63].

3. *Radiation effects and radical scission.*—Radiation stability of elastomers has been studied both with gamma radiation and in a reactor[64]. Natural rubber and most synthetic elastomers are hardened on exposure to radiation but butyl rubber and thiokol become soft and sticky. Thus both chain scission and crosslinking occur and the ratio varies with polymer type and structure. The mechanisms are not yet established although it is known that hydrogen is evolved and crosslinking could result from the combination of radicals. Cleavage may occur by disproportionation of radicals formed by the radiation as well as by attack of atomic hydrogen or other active fragments on the polymer chains. Vulcanization of elastomers by radiation has been demonstrated in a number of studies[65,66].

Cleavage of polymer chains by radical attack has been demonstrated in the reaction of natural rubber with 3,5-dibromobenzoyl peroxide. In the case of squalene and benzoyl peroxide, products were isolated which gave evidence of scission of the $—CH_2—CH_2—$ link by direct attack of a free radical[67]. Free radicals also react by abstracting hydrogen with subsequent dimerization to give crosslinks as in peroxide vulcanization.

B. RELATION OF DEGRADATION TO OXYGEN ABSORPTION

The correlation between changes in physical properties and the amount of oxygen absorbed is surprisingly good in most cases when we consider the complexity of the problem. Changes due to nonoxidative factors, as noted above, are superimposed upon the oxidative deterioration. A relatively small amount of oxygen can produce a marked change in certain properties and yet a considerable proportion of the oxygen may be consumed in reactions which do not directly affect properties. In spite of these complications, there is a proportionality between the total oxygen uptake and changes in a given property for a given stock, at least after the initial period in which the purely thermal effects are soon completed. Comparative studies usually show that a higher uptake of oxygen means greater deterioration provided one does not include major changes in type of polymer, or the nature of the cure.

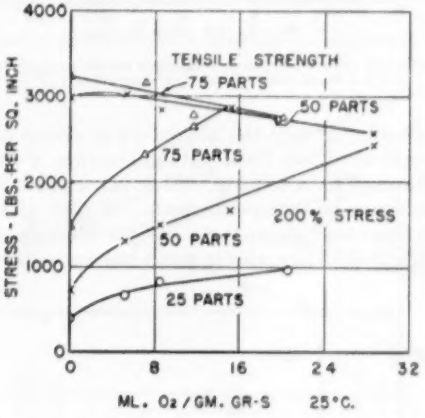


FIG. 12.—Effect of oxygen on physical properties at various channel black loadings, 100° C.

1. *Effect of carbon black and sulfur.*—A few examples from studies in which we have correlated oxygen uptake with changes in properties will illustrate the relationship. Thus in the study of the accelerating effect of carbon black on the oxidation of GR-S vulcanizates[27] it was found that the additional oxygen absorbed in a given period of time at the higher loadings produced an equivalent additional change in tensile strength as shown in Figure 12 while the accompanying increase in modulus was even greater than that produced by a similar amount of oxygen at the lower loading. Similarly, the greater oxygen uptake shown in Figure 5 for higher concentrations of sulfur in a GR-S black stock resulted in an equivalent increase in deterioration as shown by the same rate of change of modulus and tensile strength when plotted against oxygen uptake in Figure 13. A change in type of accelerator, however, altered both the rate of oxidation and the change in properties resulting from a given oxygen uptake[29].

2. *Effect of temperature and oxygen concentration.*—Changes in temperature[44] and oxygen concentration[45] not only alter the rate of oxidation but also change the ratio of chain scission to crosslinking. Scission of chains reduces tensile strength markedly and additional crosslinks introduced by oxidation may also

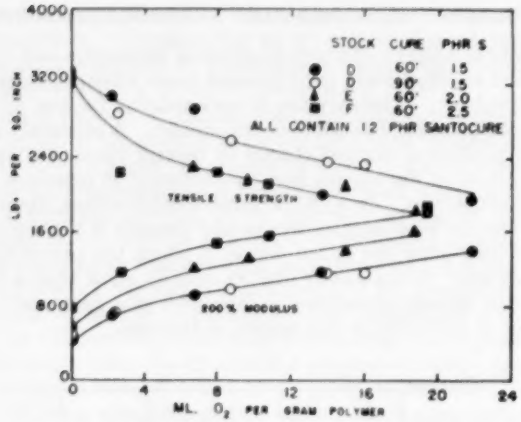


FIG. 13.—Effect of sulfur variation on changes in tensile strength and modulus of GR-S black stock with oxygen absorption, 110° C.

reduce tensile by interfering with the alignment of chains on stretching which results in crystallization. Thus the additional oxygen absorbed at the higher concentration in Figure 9 for a natural rubber black stock results in a proportionally greater decrease in tensile strength. A plot of tensile strength vs oxygen absorbed in this case[46] shows the points for aging in air and in oxygen on the same straight line. The modulus is much more sensitive to changes in the

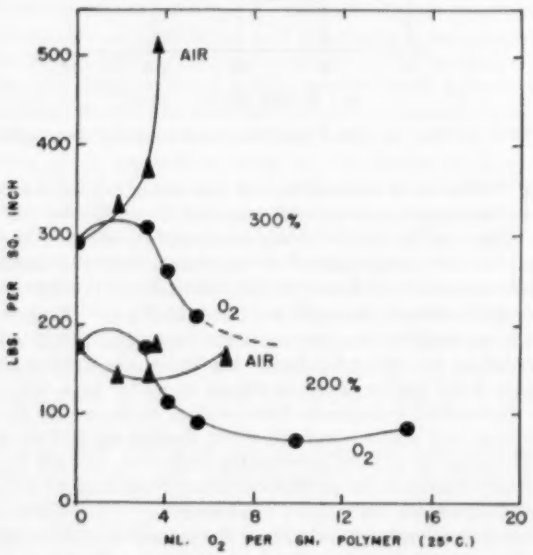


FIG. 14.—Moduli of uninhibited Hevea gum stock vs oxygen absorption in air and oxygen, 90° C.

relative amounts of chain scission and crosslinking. Figure 14 shows a dramatic example in which an uninhibited natural rubber gum vulcanizate stiffens in air and softens in oxygen. A similar change in the relative proportions of scission and crosslinking is reflected in the results of oven and oxygen bomb aging at corresponding temperatures[68].

The rate of oxygen absorption varies regularly with the reciprocal of the absolute temperature as previously pointed out in connection with Figure 8. The additional oxygen absorbed in a given time at a higher temperature produces additional deterioration, but since the ratio of chain scission to crosslinking changes, the effect upon a given property produced by a given amount of oxygen varies with the temperature. The modulus values at 200 per cent elongation in Figure 15 for a Hevea black stock show that the effect of crosslinking predominates at 50° C while at 110° scission predominates. The two effects would be balanced in this example at about 80° C. The rate of change per ml of O_2 absorbed is constant at a given temperature beyond the first 4 to 5

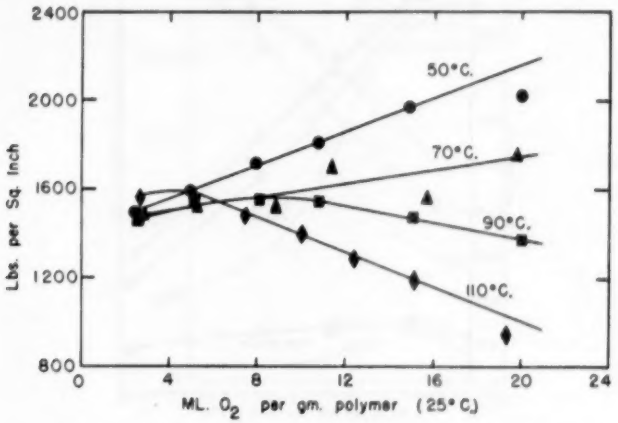


FIG. 15.—Modulus at 200 per cent elongation of Hevea black stock vs oxygen absorption at various temperatures.

ml., and a plot of the observed rate of change vs temperature gives a straight line[44]. Consequently, it is possible to establish the trend with oxygen absorption and aging data at say three temperatures and extrapolate to predict the amount of oxygen which would be absorbed at another temperature and the change to be expected in a given property. The prediction would only be valid for the specific formulation studied but the trends would apply qualitatively to any similar stock.

It is evident that one cannot use the results of an accelerated aging test at a single elevated temperature in oxygen to predict the effect upon properties to be expected from aging at another temperature in air. If, however, the effect of changes in both temperature and oxygen concentration upon the ratio of chain scission to crosslinking and the resultant effect upon properties is taken into account, a reliable qualitative interpretation of accelerated aging tests is possible.

3. *Effect of inhibitor type and concentration.*—Many antioxidants for elastomers exhibit an optimum concentration above which additional increments

result in increased oxygen uptake. A typical example was presented in Figure 10. In a majority of the cases studied[48] this optimum was confirmed by the changes in properties observed on aging. When changes in physical properties are plotted against the volume of oxygen absorbed the same rate of change is observed, as in Figure 16, showing that the extra oxygen absorbed in a given time at the higher antioxidant concentration was equally detrimental. The increased rate of oxidation could arise from increased initiation by direct oxygen attack on the antioxidant.

A few exceptions have been noted, for example, in a GR-S black stock with phenyl-2-naphthylamine a small reduction in the rate of modulus increase for a given amount of oxygen absorbed was observed in the early stages of oxidation at the higher antioxidant concentrations, but the situation reversed beyond an

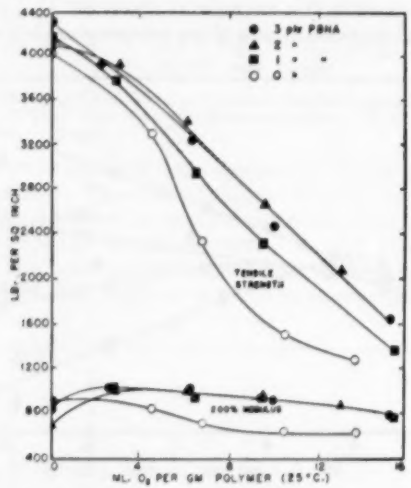


FIG. 16.—Effect of phenyl-2-naphthylamine concentration of properties of Hevea black stock vs oxygen absorbed at 91° C.

absorption of 5 ml of O_2 per gram with a greater rate of change observed for the higher concentrations thereafter[48]. A more significant exception was observed with N,N′-di-*sec*-butyl-p-phenylenediamine which showed only a small effect upon oxygen absorption (one part inhibited and three parts accelerated) and yet the inhibited stocks aged better than the uninhibited control. Even in this case, however, a given amount of oxygen was accompanied by equivalent degradation of properties so that the higher concentration was detrimental as compared with the lower, but not when compared with an uninhibited control. It was suggested that these anomalies may arise in part from the formation of radicals by attack of oxygen on the antioxidant and participation of the antioxidant radical A· in a chain transfer reaction so that a given rate of oxidation could be maintained with a lower concentration of elastomer radicals R· and RO_2· and a consequent reduction in the degradation reactions of crosslinking and chain scission.

This explanation may also apply at least in part to the behavior of mer-

captobenzimidazole which Le Bras[47] has called a "deactivator" rather than an antioxidant since it gives protection from the standpoint of properties greater than would be expected from its relatively small reduction in the rate of oxidation. The mechanism of the deactivator effect with zinc mercaptobenzimidazolate is now interpreted by Le Bras and coworkers in terms of an aftervulcanization effect during aging[47b]. Continuous and intermittent stress-relaxation measurements show that the material does not inhibit scission as originally suggested, but rather that it promotes crosslinking during aging. Thus some of the effects of scission are offset due to the formation of new crosslinks by a reaction involving free sulfur which is catalyzed by the deactivator. An earlier suggestion that the effect is related to cure[24] is thus confirmed in part, but the effect is evidently related to cure during aging rather than merely to the initial state of cure.

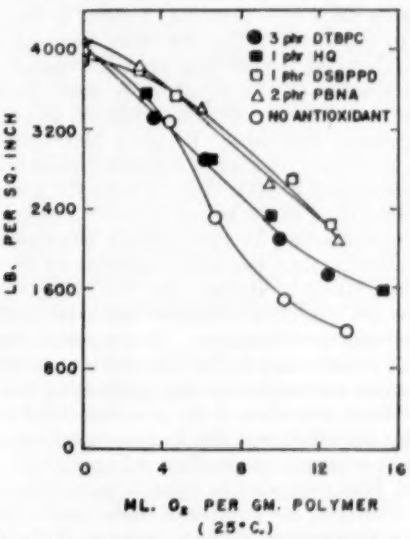


FIG. 17.—Variation of tensile strength of optimum concentration of antioxidants in Hevea black stock with oxygen absorption at 91° C.

Different types of inhibitors give somewhat different amounts of degradation for a given oxygen uptake. In Figure 17, for example, the stocks with amine antioxidants follow one curve for changes in tensile strength, and those with phenolic antioxidants give a somewhat different curve, while the uninhibited control exhibits a still different behavior.

It was pointed out in the discussion of antioxidant action that a given antioxidant may function in more than one way to alter the rate of oxidation. The net effect upon physical properties will vary depending upon the relative magnitude of the competing reactions. Thus while oxygen-absorption data usually make it possible to select the best prospects in a comparative study of antioxidants, it is also important to measure changes in physical properties in order to detect the unusual cases in which protection against change in certain properties may be obtained without a proportional reduction in the rate of oxygen uptake.

C. STRESS RELAXATION AND CREEP MEASUREMENTS

Studies of continuous and intermittent stress relaxation and creep are particularly useful in interpreting the contribution of crosslinking and scission reactions to the degradation of properties of elastomers. Intermittent methods in both cases are merely periodic measurements of the modulus. In the one case the sample is always stretched to the same elongation and the stress measured, while in the other the same stress is applied each time and the elongation measured. Both methods measure the net effect of scission and crosslinking and give the same curve when plotted in an equivalent way in terms of equations relating the stress-strain data to the number of network chains as derived from statistical theory[69].

Continuous stress-relaxation measurements at constant elongation in the presence of oxygen at elevated temperatures give a direct measure of the effect of chain scission since new crosslinks formed in the stretched condition do not contribute to the stress. The difference between the continuous and intermittent stress-relaxation curves thus gives a measure of the contribution of the crosslinking reaction. The situation is more complex in continuous creep measurements since the new crosslinks formed at any time begin to contribute as the elongation increases. Relating intermittent and continuous stress relaxation to the actual number of network chains using equations based on the fundamental equation of state derived from the kinetic theory of rubber elasticity permits calculation of the actual rates of crosslinking and scission[3].

A method of superimposing an intermittent measurement upon the continuous stress-relaxation method has been employed by Ore[70]. Using the same sample, an additional stress is applied and the elongation measured. New crosslinks formed in the stretched condition will contribute to the additional stress required to increase the elongation. It is reported that this method gives the same measure of crosslinking as the intermittent method and offers some advantages. The same author found that preheating the samples markedly reduced the initial rate of relaxation of the peroxide-cured vulcanizates studied. It was suggested that the effect was due to decomposition of rubber hydroperoxides that formed on exposure to air after vulcanization.

Stress-relaxation data may also be related to oxygen absorption and this provides a method of relating the number of chain cuts to the amount of oxygen absorbed. Based on an assumed random cleavage, Tobolsky and coworkers[14] report that the ratio varies with temperature in thermal oxidation with as many as 30 moles of oxygen absorbed per chain cut at 75° C, while at higher temperatures (120–130° C) and with photoactivation even at lower temperatures (so that maximum rate conditions are approached), the ratio is nearly unity. Similar values have been reported by other workers[71] in spite of some criticism of the validity of some of the theoretical assumptions.

These and other tools are bringing us closer to an understanding of the fundamental aging reactions of chain scission and crosslinking. The application of stress-relaxation data to the question of the mechanism of scission will be considered in the discussions which follow relative to the available information regarding the nature of these reactions which are responsible for the degradation of properties of elastomers on aging.

D. MECHANISM OF CROSSLINKING

Reactions which result in the joining together of polymer molecules are fairly well understood even though the exact mechanism is not yet established

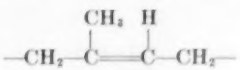
for the aging of elastomers. These reactions include the combination of free radicals, the addition of radicals to double bonds, and in some instances, a vinyl-type polymerization.

Peroxide vulcanization of elastomers illustrates a case in which it is believed that two polymer radicals join to form a crosslink. The radicals formed by decomposition of the peroxide abstract hydrogen atoms from the polymer molecules to form free radical points on the chains. When two such reactive centers come close enough together they readily combine to form a covalent bond:

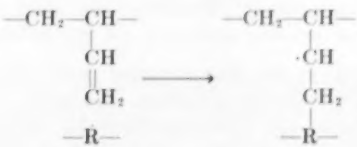
$$RH + RO\cdot \longrightarrow ROH + R\cdot$$
$$2R\cdot \longrightarrow R{-}R$$

Free radicals formed by hydrogen abstraction in the oxidation mechanism can combine similarly to form crosslinks. The effect of oxygen concentration on the ratio of crosslinking to scission provides evidence of the participation of $R\cdot$ radicals[46]. The stiffening effects of crosslinking predominate at lower oxygen concentrations, while at higher oxygen concentrations which would favor conversion of $R\cdot$ to $RO_2\cdot$ the scission, reaction becomes of greater importance.

A free radical can add to a double bond to form a new radical which could combine with another radical as above, lose a hydrogen atom to reform the unsaturation, combine with O_2, or if conditions are favorable, initiate a vinyl-type polymerization. The stiffening of the synthetic butadiene-styrene rubbers on aging as compared to the softening of natural rubber during accelerated oxidation reflects the effect of structural differences upon the ease of addition of free radicals. The internal double bond of the 1,4-isoprene unit with its side methyl group is so hindered by the groups attached that free-radical addition is difficult:



In contrast, the side vinyl groups formed by about 20 per cent of 1,2-addition in a typical emulsion polymerization provide favorable sites for crosslinking by addition of polymer free radicals at the unsubstituted end of the double bond:



Oxy radicals may also add to a double bond or combine with a radical to form ether links (in the case of $RO\cdot$) or peroxide links (in the case of $RO_2\cdot$). Polymeric peroxides have been obtained in some cases from olefins[8]. Studies of hydroperoxide yields[72] in the autoxidation of olefins show that in some cases $RO_2\cdot$ must add to double bonds since not all of the oxygen absorbed is accounted for as ROOH and by scission. The proportion of such addition increases as the reactivity of the alpha C—H decreases. However, the $RO_2\cdot$ radical is much more inclined to react by hydrogen abstraction to propagate the oxidation cycle and ultimately to produce scission rather than crosslinking.

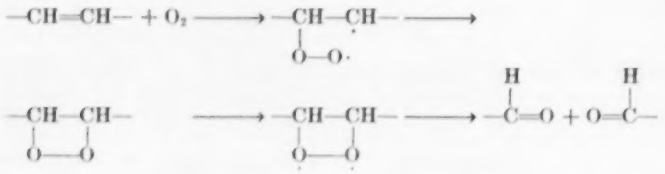
The mechanism of crosslinking seems to be associated primarily with re-

actions involving carbon free radicals formed on the polymer chain during exposure to the aging atmosphere whether it be oxygen, heat, light, radiation, or combinations of these deterioration factors. Carbon black also plays a part in the formation of additional crosslinks during aging, apparently by combination with R· radicals to form a bond between the elastomer molecule and the carbon particle. Evidence for such a free radical interaction between carbon black and rubber is provided by a recent study by Watson[73]. A decreased reinforcing ability on treating the black with $K_2S_2O_8$ is attributed to a reaction with ·OH radicals. (Carbon black-rubber interactions are discussed in another paper in this first issue of Rubber Reviews.)

E. MECHANISM OF CHAIN SCISSION

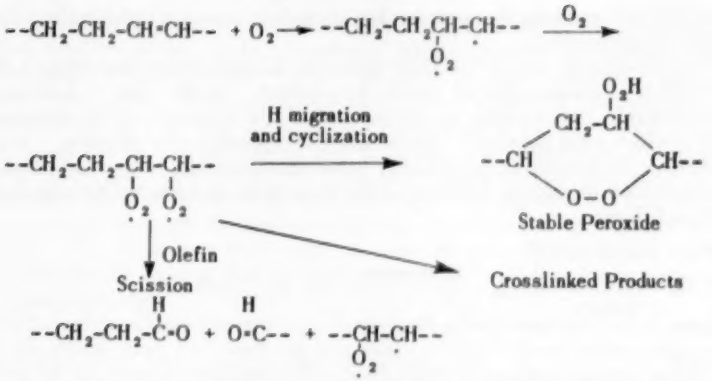
The mechanism of chain scission of elastomers has been the subject of numerous studies. Several possible scission mechanisms have been suggested but the typical mechanism of oxidative scission has not yet been established. One question of importance is whether the scission reaction is involved directly in the primary mechanism of oxidation, or whether it is a side reaction, or a subsequent reaction involving the products of the primary reaction. In the absence of conclusive evidence we will consider some of the possibilities.

Products of oxidation of simple olefins showed evidence of scission by direct oxygen attack at the double bond as well as at the alpha methylene[15,18,20]. Initiation of oxidation by direct oxygen attack at the unsaturated center is said to increase with temperature until it predominates at 100–120° C[3,74]. A mechanism for scission by direct oxygen attack on the double bond can easily be represented as involving the transient formation of a four-membered cyclic peroxide which undergoes homolytic cleavage to a diradical which readily splits to give scission of the chain:



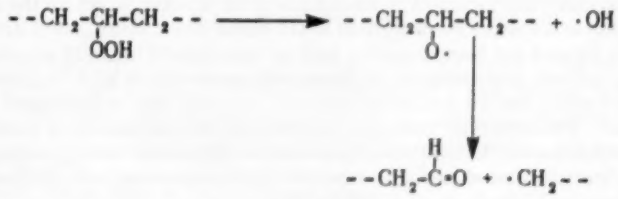
This cyclic structure was at one time accepted as the probable structure of the peroxides formed in the oxidation of olefins. No proof of the existence of such a structure has been found and it was subsequently established that hydroperoxides are the main primary product. Reduction of olefin peroxides does not give the 1,2-diol that would be expected from the cyclic structure and consequently, if such an intermediate is formed, it must immediately undergo scission as indicated[3,75].

An intersting mechanism for scission has been proposed on the basis of an observed close relationship between changes in the degree of unsaturation, number of scissions, and formation of peroxides in the oxidation of GR-S in solution[76]. The observed behavior is accounted for by the formation of a diperoxide diradical intermediate which can undergo scission, give crosslinking, or form a stable cyclic diperoxide identical to the structure which Bolland[8] obtained by a different mechanism.



The final scission mechanism is not too convincing, but the idea that scission may involve direct O_2 attack on the double bond, independently of the primary oxidation mechanism, deserves continued consideration. The scheme involving the transient formation of a four-membered ring as discussed previously is a simpler application of this concept.

If scission is considered to result from peroxide decomposition, the simplest approach involves a homolytic cleavage to form RO· which disproportionates to give scission products:

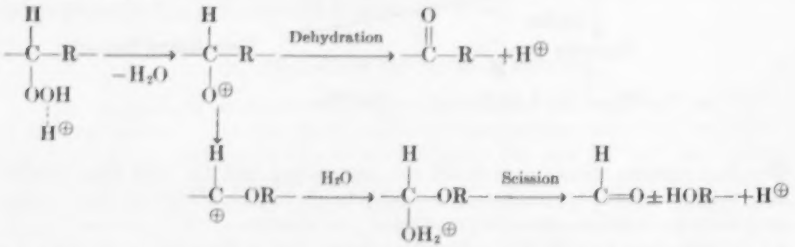


Tertiary peroxides appear to decompose by such a mechanism to give a ketone and a radical[13]. This same homolytic cleavage is involved in the initiation of oxidation by peroxide decomposition and if it is also responsible for scission, any major change imposed upon the initiation process would alter the scission efficiency.

The possible location of the scission reaction, in the initiation, progapation, or termination steps, has been studied by measuring the scission efficiency (ratio of chains cut to moles O_2 absorbed) under varying conditions[77]. No change in the proportion of scission was observed with different initiators and so it was concluded that scission is not involved in the initiation stage. This would seem to eliminate scission by way of the RO· radical. Similarly, addition of inhibitors to alter the nature of the termination process did not change the scission efficiency. It was thus concluded, by a process of elimination, that scission must involve the propagation stage. The choice between R· and RO_2· is fairly obvious since in the presence of oxygen R· is rapidly converted to RO_2· and the effects of scission are more pronounced at higher oxygen concentrations[46]. It should be remembered that this evidence that scission is associated with RO_2· is based on negative evidence and a process of elimination and that no direct connection between RO_2· and scission has been demonstrated. The

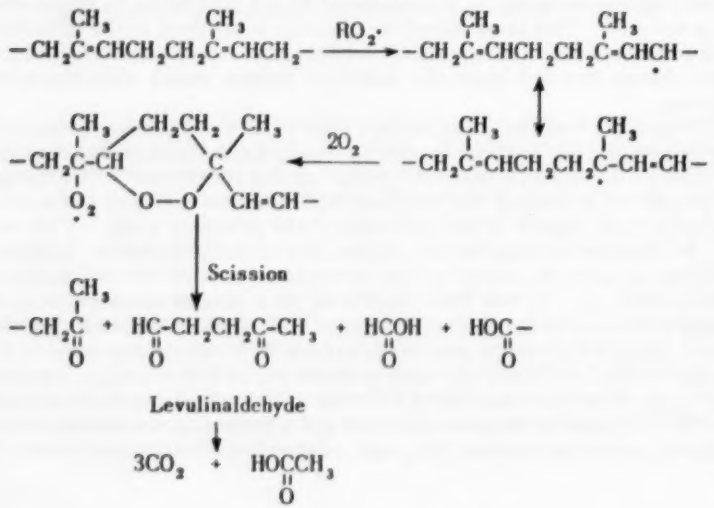
possibility still remains that scission is a secondary reaction outside the primary oxidation mechanism.

The possibility of a heterolytic peroxide decomposition involving a polar mechanism of scission should not be overlooked. In the case of a secondary hydroperoxide, dehydration to a ketone would be expected in the presence of acids or other polar catalysts, with scission as a possible side reaction. A polar mechanism for scission in this manner based on an analogy to the acid-catalyzed decomposition of cumene hydroperoxide to acetone and phenol may be formulated as follows:



In the case of a tertiary hydroperoxide, formed by attack at a tertiary C—H resulting from 1,2-polymerization of a diene, the breaking of a C—C link in a polar decomposition would inevitably result in cleavage of either the main chain or side chain.

Bevilacqua[78] has formulated a mechanism for scission based on the products of oxidation and oxygen consumption in the oxidation of latex and of dry rubber. The acids formed are formic, acetic, and carbon dioxide in stoichiometric ratios of 1:1:3. From the amounts of these scission products and the oxygen absorbed per chain cut he concludes that one isoprene unit is destroyed for each chain cut. The observed behavior is explained on the basis of a modification of the mechanism of Bolland[8] in which a cyclic diperoxide (or the corresponding $RO_2\cdot$ radical) is formed and decomposed to give the observed products which include levulinaldehyde as an intermediate:



The question is frequently raised as to whether scission is a random process or if it is directed at or near the crosslink. Arguments for both points of view have recently been presented[79,80] based on stress-relaxation studies. Horikx[81] computed the number of scissions from the fraction of soluble material in a degraded network and related the scission to the number of effective chains between crosslinks in a three-dimensional network. He found that the scission reaction accompanying oxygen absorption in a natural rubber-sulfur-Santocure vulcanizate at 100° C does not involve opening of the crosslinks. It remained undecided as to whether the scission is random or directed in the vicinity of the crosslink. Recent studies by Veith[82] on chain scission and oxidation rates is interpreted on the basis of Bueche's theoretical analysis[83] to indicate a nonrandom scission process.

Bevilacqua[5] suggests that scission occurs both at the crosslink and at random along the chain since the observed behavior usually falls in between the predictions for the two alternatives. The mechanism of random scission along the chain would be the same as for the unvulcanized polymer while the scission directed at or near the crosslink has not yet been explained.

It is evident that more than one mechanism of scission is possible. Different mechanisms may predominate with changes in the nature of the elastomer and the conditions of oxidation. Even in a given material under a given set of conditions competing reactions may proceed simultaneously. Further reaserch is clearly necessary to establish the mechanisms by which crosslinking and chain-scission reactions occur in the oxidation of elastomers.

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THE VULCANIZATION OF RUBBER WITH SULFUR

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I. INTRODUCTION

E. H. Farmer[1] compiled a review of *vulcanization* which was published in 1946 as an important chapter in Volume II of "Advances in Colloid Science". About two years later, Normann Bergem[2] published a review under the same title. These authors dealt with the subject from rather fundamental points of view, but, because of more recent work from many laboratories and the increasing importance of elastomers, a fresh survey seems warranted. Accordingly, the present review aims to bring a part of the subject up-to-date. The viewpoint taken differs from those of Farmer and Bergem in some respects which seem rather important. For example, emphasis will be placed on the various rates of reactions including those of the scorch and reversion periods and on the importance of possible intermediates such as hydrogen sulfide and suitably terminated sulfur chains.

The kinetic theory of elastomeric behavior constitutes the background against which any current treatment of vulcanization should be developed. Actually, vulcanization is a part of this background. Thus, Busse[3,4] considered the following conditions necessary for the existence of rubberlike elasticity: (1) the presence of long chain molecules with freely rotating links, (2) the presence of weak secondary forces between molecules, and (3) the crosslinking of molecules into a three dimensional network. The three conditions taken together, at least in present day thinking, imply that long range elasticity results from the kinetic activity of segments which resembles yet differs from the kinetic activity of gas molecules. A segment is composed at most of only a few monomer units and is terminated at either end with another segment, a crosslink or an endgroup. When terminated with an endgroup, its kinetic activity may even detract from network behavior and then it is a defect. When terminated by a crosslink or another segment it is an integral part of the network and as such can contribute to the overall elasticity. It is more or less obvious that segments terminated by crosslinks and the crosslinks themselves should dis-

play an activity different from that of segments distant from crosslinks. Crosslinks, though relatively massive, are expected to move in a limited way (microBrownian) as a result of the kinetic activity of nearby segments. Crosslinks are necessary but are thus a sort of network defect. Those of lower functionality probably can contribute beneficially to the overall kinetic activity.

Small molecule compounds often are used to advantage in the study of crosslinking, a process that is broader than vulcanization. Squalene, with six isoprene units, linearly connected and terminated in hydrogen, obviously might display behavior assignable to the cooperative action of two or more adjacent isoprene units. As such it is convenient for certain physical and chemical studies. However, like other small-molecule compounds, it contains a high weight percentage of endgroups. This makes difficult any deductions based on results on the crosslinking of it in the study of the crosslinking (vulcanization) of a rubber, say with 1000 or more segments. The crosslinking of small molecules will not be considered in much detail in this review since the reviewer feels that the type of kinetic activity prevailing when the segment is a part of a long chain can never be displayed by a small molecule.

Vulcanization within the perspective of the kinetic theory may be defined as the chemical reaction in which segments of separate elastomer chains are joined with each other in such a way that a three dimensional network is produced. The primary molecular weight, the crosslink density, and the spacing of crosslinks with respect to each other are important features as are the strength of the crosslinks with respect to the strength of the links in the main chains. The composition of crosslinks is not an essential property just as the composition of the main-chain segments is not essential to long range elasticity. It will be seen that the joining of the long molecules is not exclusively crosslinking, but that chain extension, segment interchange, branching (this may be considered trifunctional crosslinking), and chain scission are, or, may be important features of the vulcanization process.

Crude NR is usually not free of crosslinks[31] and, further, may be of such high molecular weight that the entanglement of the long chains may create virtual crosslinks. Uncured rubber is thermoplastic, cured rubber is much less so. In general, for the ordinary low molecular weight elastomers, there is no insurmountable problem of distinguishing the vulcanized from the unvulcanized condition. The most common and reliable method is based on the fact that low molecular weight unvulcanized rubbers dissolve in suitable solvents whereas vulcanized ones merely swell. The degree of swell is for practical work a sufficiently quantitative measure of kinetically active chain concentration, or of crosslink concentration, or of state of cure. However, stress-strain measurements may seem more revealing, as for filled stocks. Even for gum stocks they are often more convenient and only slightly less quantitative, especially if the data are limited to modulus at low extensions and if creep is effectively allowed for (often merely ignored).

The chemistry of vulcanization deals with the composition of the starting materials, the mechanisms by which they react, and the composition of the vulcanizates.

In this review crosslinking will be dealt with at some length but the preceding, simultaneous or subsequent reactions of chain extension, chain scission, chain branching, cyclization, crosslink breakage and crosslink transfer will also be considered. It is now fair to say that these reactions occur in such a way that three stages of vulcanization often are clearly evident even though the chemistry involved is not. These three stages are the delayed action or scorch

period, the cure period, and the overcure or reversion period. It should be possible to define vulcanization in purely empirical terms. In the final section a definition will be attempted which aims to utilize empirical knowledge of the chemistry and physics of the process and which avoids any conflict with kinetic theory.

The kinetic theory includes the relation of the force of retraction, F, to the extension ratio, α, by the expression:

$$F = \frac{dRT}{M}\left(\alpha - \frac{1}{\alpha^2}\right)$$

Here, d is the density, R the gas constant, M the average molecular weight between crosslinks, and T the absolute temperature. The organic chemist may accept and use such formulations though he may feel that they have limited application. And, anyway, the exact formulation is quite outside his field. Obviously such formulation should be considered by another reviewer if, indeed, it is in need of review at all. See, for example, Flory[5] "The Principles of Polymer Chemistry" and Treloar[4] "The Physics of Rubber Elasticity". A comprehensive application of the kinetic theory to filled vulcanizates has been given by Kraus[6] under the title "Degree of Cure in Filler-Reinforced Vulcanizates by the Swelling Method".

The compounder's experience with unsaturated elastomers teaches that sulfur is the most effective general-use vulcanizing agent. Its action depends on accessory materials of which there are several classifications. The most important of these are *accelerators*, both organic and inorganic. *Activators* are of two main types: metallic oxides and fatty acids. Of these zinc oxide is the most important oxide and stearic acid the most important acid. Primary or secondary aliphatic amines are sometimes used as activators. Finally, *retarders* are an important classification. These are of two broad types: radical reagents and acidic materials.

Vulcanization by radiation was reported in the thirties by E. B. Newton[7a], was treated in some detail by Farmer[1] (1946), and by Stevens[8] (1946) under the headings *photovulcanization*, *photogelling*, etc. According to Gehman and Auerbach (1956) it has little technical promise but has considerable value to the theory or rubbers[7b].

Recently, two nearly all-*cis*, 1,4, head-to-tail polyisoprenes, Ameripol SN[9] and Coral[10] rubber, have been reported. The curing of these as well as of several other polymers is of interest and has further revealed how complicated the study of vulcanization really is. Where such curing is effective for clearing up a particular point, it may be mentioned in some detail but the full discussion of the vulcanization of neoprene, IIR, SBR, silicone, thiokol, NBR, etc. would be too great in scope for this review.

The mechanisms of vulcanization are becoming more evident as our knowledge of elastomers in the cured and uncured states becomes more definite. As expected, the kinetics of the various crosslinking procedures have not thus far told very much about the mechanisms. They are fundamental in their own right, however, and do contribute to the overall understanding and to the use of vulcanization. Two sections will be devoted to various rate studies.

The vulcanization of filled stocks will be treated only incidentally because this field is a part of *reinforcement* to be considered in other reviews[11].

Since Bergem's review[2], the findings of several groups have indicated the nature of endproducts formed from some of the rubber chemicals during vul-

canization, including those from sulfur, TMTD, zinc oxide, MBT, MBTS, etc. A knowledge of them helps in understanding the stages of vulcanization: scorch, cure and reversion.

The self-limiting effects in vulcanization are quite interesting and appeared worthy of mention in various sections.

The contention that vulcanization[1,2,5] is unusually complicated and poorly understood is widespread. This is scarcely justified. Surely, no one familiar with such a broad field expects complete understanding. It would appear that numerous polymer chemists and physicists, if they chose to make the effort, could show that the kinetic theory of elastomeric behavior is doing rather well as a basis for systematizing the facts of vulcanization.

The abbreviations[12] for the various elastomers which will be used are those of ASTM Committee D-11. They are:

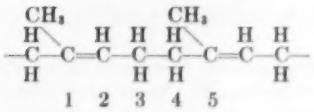
BR – Butadiene rubbers
IR – Isoprene rubber, synthetic
CR – Chloroprene rubbers
NR – Natural rubber
ABR – Acrylate-butadiene rubbers
IIR – Isobutene-isoprene rubbers
NBR – Nitrile-butadiene rubbers
PBR – Pyridine-butadiene rubbers
SBR – Styrene-butadiene rubbers
SCR – Styrene-chloroprene rubbers
SIR – Styrene-isoprene rubbers

Other abbreviations to be used include:

MBT – Mercaptobenzothiazole
MBTS – 2-Benzothiazolyl disulfide, the disulfide corresponding to MBT
DMADC – Dimethylammonium dimethyldithiocarbamate
TMTM, TMTD, TMTtri, TMTtetra – Tetramethylthiuram mono-, di-, tri- and tetra-sulfides, respectively
TETM, TETD – Tetraethylthiuram mono- and disulfides
ZnDMDC, ZnDEDC – Zinc dimethyl- and diethyldithiocarbamates, respectively
PBNA – Phenyl-2-naphthylamine
phr – parts per hundred of rubber
psi – pounds per square inch
ASTM – American Society for Testing Materials
BRPRA – British Rubber Producers' Research Association
RABRM – Research Association of British Rubber Manufacturers
ACS – American Chemical Society

II. THE CROSSLINK PRINCIPLE AND THE STRUCTURE OF NATURAL RUBBER

C. O. Weber[13], prior to about 1900, expressed the opinion that NR molecules are long (relatively short by present knowledge) open chains, a view which he may have held for many years. Pickles[14], owing to the ozonolysis results of Harries[15], was able to formulate the Weber structure more precisely. The now familiar 1,5-diene formula (i.e., the 1,4 head-to-tail formula) for polyisoprene approximates the Weber-Pickles structure. Taking the isoprene units two at



a time, NR thus is a poly 1,5-diene. The double bonds have the *cis* configuration as proposed first by Meyer and Mark[16,17] and the units are arranged head-to-tail. The concept that rubber is of very high molecular weight, i.e., of *macro* molecular weight was contributed by Staudinger. The most concise way of expressing the structure of rubber is to say that it is the structure of high molecular weight, all-1,4, all-*cis*, all-head-to-tail polyisoprene. From this the Weber-Pickles formula may be drawn and the 1,5-dienic feature of the structure then will be evident.

The molecular weight and molecular weight distribution are important variables for NR as for any soluble high polymer. When taken from the tree it may have a molecular weight[18] of several millions and each particle of the latex may contain only a single molecule. When this is the case the polymer is not soluble. Quoting Bateman and Watson[18] we find that "Critical studies by Gee . . . finally established that raw rubber, as known in Europe, has a mean molecular weight of 350,000". During most plantation, laboratory, or factory processing the molecular weight is reduced, and, when the time for vulcanization has arrived, a value of less than 200,000 is probable. Lack of solubility in raw rubber may also be due to the presence of occasional crosslinks as well as to the property of high molecular weight. Most good quality raw NR thus appears to be weakly crosslinked. Little seems to be known about how the molecules are formed, with respect to each other, i.e., whether they are formed singly or in groups and, if in groups, if the groups have a head-to-tail arrangement corresponding to that of the individual molecules. Rubber crystallizes fairly easily and has an equilibrium melting point[19] of 28°, but in no case does the crystalline fraction constitute more than about 0.35.

The pin-splitting test of Andrew Szegvari[20] is of interest in attempting a description of rubber. This test can be done conveniently with a sheet of rubber 0.025 inch thick which may be deposited from latex. As such it will not have been mechanically degraded. When stretched several hundred per cent, it can be split easily by passing a pin through it in the direction of stretch but splitting cannot be made to occur at right angles to the direction of stretch. The direction of stretch may be selected at random. Such behavior is accounted for nicely by the three requirements for long range elasticity, including segment action, as given in the introduction. This test must be affected to some extent by the remnant latex particle structures, but since the test is given by suitably high molecular weight samples of butyl, smoked sheet and pale crepe rubbers, it is not due primarily to such remnant structures. The pin-splitting test may suggest too readily that the structure of rubber is simply a structure of a collection of *individual* molecules. Such a structure might be based on the possibility that rubber molecules may act in groups whether or not they were formed that way initially. Thus, Mooney[21] has suggested that the flow of rubber can be accounted for on the basis of *collections* of whole molecules rolling over each other. However, in the present discussion, it is often assumed that any specimen of uncured rubber is a collection of individual molecules, the segment action of which accounts for the behavior of the specimen without any group action being involved. Cured specimens fail to split in the

test, which behavior may be considered as fairly direct evidence for the presence of crosslinks.

The functionality[22] of crosslinks is important, at least theoretically. Thus, three, four, five, or more molecular chains may emanate from a more or less inextensible or nondeformable region in the network. The number may conveniently be called the *functionality* of the crosslink. It seems likely that the functionality of most of the crosslinks introduced into natural rubber by milling is three, i.e., they are branches. The usual assumption, by no means proven, is that vulcanization usually introduces tetrafunctional crosslinks. The term[5] "giant crosslink" is often applied to a crystallite or filler particle which acts as the inextensible region binding many chains. Twiss[23] tried to achieve reinforcement by vulcanization without much success, but if he could study in this respect some of the present-day urethans, he might conclude that their excellent rubbery properties are due in part to the proper concentration, distribution, and functionality of the crosslinks. However, he would be faced, even today, with a lack of methods for expressing and measuring these properties.

Bergem[24] reviewed X-ray spectrography as a tool for getting at the fine structure of elastomers. Probably it deserves greater use in the study of vulcanizates.

The structural characteristics of the sulfur linkage in natural rubber vulcanizates have been summarized by Bateman, Glazebrook, Moore, and Saville[25]. They state that vulcanizates do not contain solely open chain diisoprene units linked in an alkyl-alkenyl polysulfide structure, but that tetrahydrothiophene structures are incorporated at points adjacent to the crosslinks. Much progress has been made by the BRPRA workers, but apparently the structures in the vicinity of crosslinks are still in doubt.

The mechanism by which such structures are formed is polar according to Bateman and coworkers. This constitutes a revision of the view previously put forward by Farmer and his associates who believed vulcanization to be radical in nature. The important point to be made here is that the knowledge of these structures, proposed and studied by the groups of workers at BRPRA, constitutes a large part of what we know about vulcanizate structure. They discuss adequately the possibility that some of the vulcanizing agent may be consumed in forming five and six-membered rings. These structures must constitute network defects and so their formation constitutes side reactions to the reaction of interest.

Even though vulcanizate structure in the vicinity of crosslinks is uncertain, the formulas of Figure I may be of value, at least for discussion. Structures with C—C crosslinks[26] having formulas 1 and 2 are expected in radical cured vulcanizates, for example, in *tert*-butyl or cumyl peroxide NR cures. They may even be present in sulfur cures. Structures of formulas 3 and 4 are expected in sulfur cures. It would be out of place to argue here the evidence for these and other structures for vulcanized rubber. Structures 1 and 3 do not involve a loss of hydrogen whereas the formation of 2 and 4 involve the loss of two hydrogen atoms per crosslink. The stoichiometry of crosslinking, including the number of sulfur atoms in crosslinks, will be discussed in Section VI. For trifunctional crosslinking see also the following section on Scission Effects.

III. SCISSION EFFECTS DURING THE SCORCH PERIOD

This section considers the possibility that polymer scission effects may account for all or part of the induction or scorch period of the vulcanization

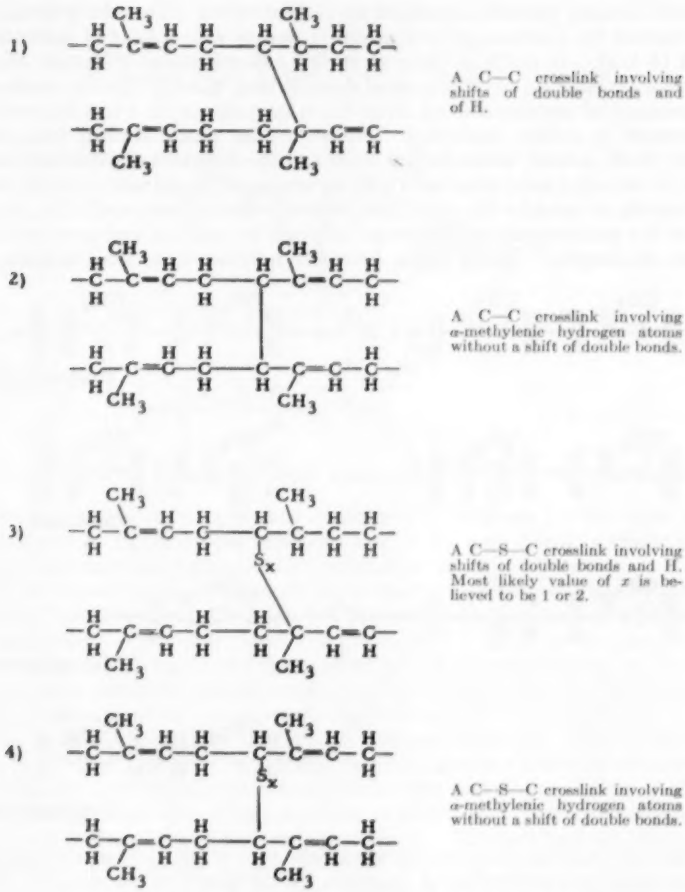
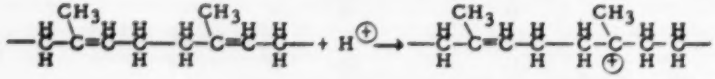

1)
A C—C crosslink involving shifts of double bonds and of H.
2)
A C—C crosslink involving α-methylenic hydrogen atoms without a shift of double bonds.
3)
A C—S—C crosslink involving shifts of double bonds and H. Most likely value of x is believed to be 1 or 2.
4)
A C—S—C crosslink involving α-methylenic hydrogen atoms without a shift of double bonds.

FIG. 1.—Some possible structures of tetrafunctional crosslinks.

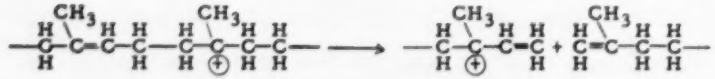
process. Alternative approaches assume the delay in the overall process to involve only nonpolymer molecules, vulcanizing agents, activators, retarders, reactive intermediates, etc., or the action of these components on the rubber. They will be discussed briefly in later sections.

Recently, Watson[27] reported on the *in vacuo* degradation of unpurified natural rubber solutions. The naturally occurring antioxidants, stabilizers, and activators (if any) were purposely not removed prior to his studies. The degradation which took place at the same rate in air as *in vacuo* was followed viscometrically, a final limiting viscosity being attained. It was believed to be nonoxidative in nature since the addition of hydroquinone or of oxygen, or the removal of natural antioxidants, or the increase in hydroperoxide content, all had no effect. However, weak organic acids, even acetic acid, were found to be active catalysts. The addition of quinone or of thiophenol to a solution having

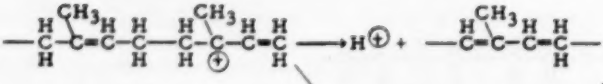
the final limiting viscosity produced no further effect. The effect of temperature showed the reaction to be thermal in nature with a heat of activation of about 16 kcal. It was first order in rubber concentration. Watson offered a tentative explanation for this type of degradation, namely, that it results from the breakage of occasional weak links which he suggests (as a new feature) may be present in rubber molecules. However, the much studied behavior of rubber, itself an acid, toward other acids and the behavior of extracted rubber, which is free of at least some naturally occurring acids and antioxidants, makes it advisable to consider the possibility that the reaction is merely the protonation of the polyisoprene double bond followed by scission and termination by proton elimination. These steps, hereafter referred to as ionic scission, are:



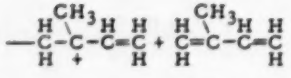
Protonation



Scission



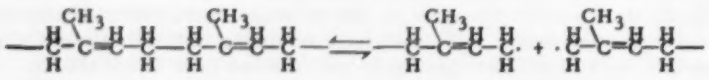
Termination



Depropagation

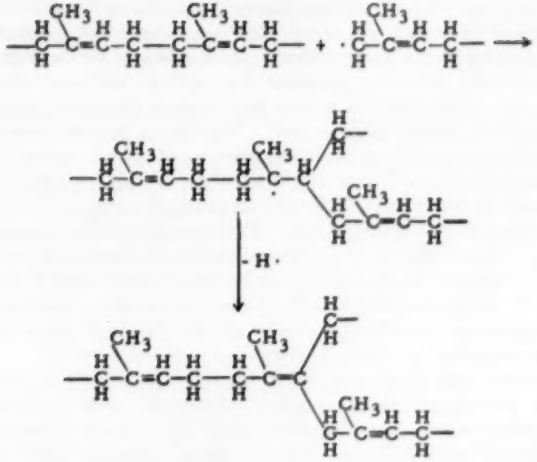
The ionic scission step is a depropagation step in the more or less hypothetical cationic polymerization of isoprene. Depropagation to isoprene is also shown.

Alternative to ionic scission in the behavior of polyisoprene is one or more radical processes. It is usually considered that the weakest link[41] in the NR chain is that between the methylene groups. For example, this bond is probably the one which breaks and reforms most frequently during the milling of rubber:



The radicals apparently do not all recombine. Some are believed to undergo hydrogen transfer to form hydrogen terminated short chains and internally situated radical sites on contiguous chains. Dimerization would then lead to the usual tetrafunctional crosslink. Some of the scission-produced radicals no doubt undergo endlinking with double bonds to produce trifunctional crosslinks

as follows:



Such processes may have been considered by Watson for the spontaneous degradation of dilute rubber solutions but, if so, were possibly discarded because of the insensitiveness of the degradation to radical reagents.

With respect to the stability of dilute solutions of polyisoprene the findings of Golub[28] are of value. He studied NR and Alfin polyisoprene of high molecular weight and as stabilizer used one per cent of TMTD on the polymer, the effectiveness of this agent in Alfin rubbers having been first noted by Diem and by others in extracted natural rubber. Golub found the TMTD containing solutions of natural rubber of about two million molecular weight and of Alfin polyisoprene of about three and one-half million molecular weight to be stable in air for several months. Weak links were not apparent under these conditions. The NR, of course, contained naturally occurring fatty acids. Now, TMTD is not known to react with dilute solutions of weak acids, but it is a vulcanizing agent and is often held to be a radical reagent. The fact that the dilute solution scission effect is not, on the one hand, solely an effect of dilute acids and, on the other, is not purely of a radical nature, as disclosed by insensitiveness to oxygen, may suggest that the effect can involve simultaneously both ions and radicals.

Bergem[29] reviewed the thermal stability of the polyisoprene molecule. He, like Farmer[30] and numerous others, considered the weakest link to be that between the methylene groups. He estimated the heat of fission there to be only 43 kcal. Of considerable importance too, he pointed out that it is reasonable to expect instability to increase with chain length. And, further, he considered the introduction of crosslinks to increase stability as a result of shortening the chains (chains between crosslinks). Borrowing an expression from the kinetic theory of gasses

$$\frac{n}{n_0} = e^{-E/kT}$$

where, for linear polymers, n = the number of links per unit volume having the minimum energy E to react, n_0 = the total number of chains per unit volume,

k is a constant, and T the absolute temperature, he considered n/n_0 to be a measure of the possibility of chain scission (cuts per molecule) or of the possibility that sufficient energy can accumulate in a single link to break it. Other comments made by Bergem were that van der Waals forces will increase the chances of scission. Swelling pressure was said to aid chain rupture. Bergem's treatment, which here is called the *scission principle*, appears to make Watson's weak-link theory unnecessary. Both seem to emphasize the possibility of chain scission during any chemical reaction of rubber, including vulcanization. The crosslinking of NR on standing while drying, reported on by Wood[21] and commented on by Watson[27], should be studied in connection with the section on the chemistry of crosslinking. Van Amerongen[32] commented on thermal stability: "One difference [between bulk and dissolved rubber] is that changes to be observed in dry rubber on heating to 200–225° C begin to occur at 100–120° C in rubber solutions". Based on molding studies *in vacuo*, in nitrogen, and in air of deproteinized crepe at 140° Mullins[76] found it impractical to avoid some degradation during cure.

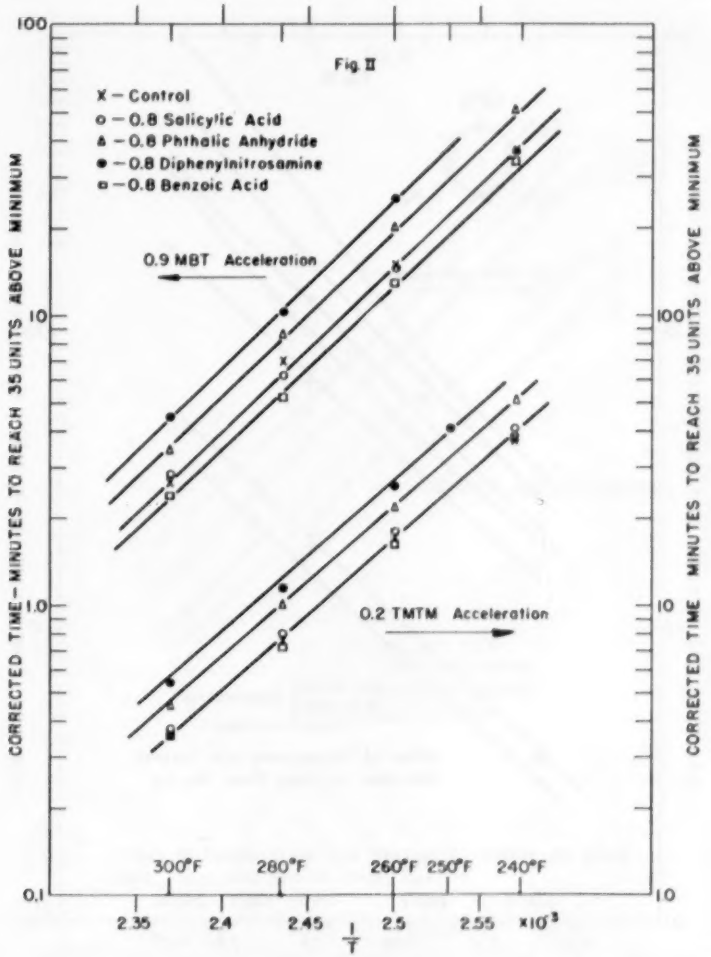
The Chemistry and Technology of Rubber[23,67] contains four chapters dealing with various aspects of vulcanization. Especially well reviewed were the effects of accelerators and vulcanizing agents other than crosslinking effects. In 1934 Williams[20] proposed that rubber "units" combine with sulfur to form simpler units, R′ and R″S (Zapp[72] later made a related suggestion). The union of R′ units as the third and final step was believed to form the vulcanizate. Thus, he clearly stated conditions for scorch and cure periods that are similar to the views set forth in the present treatment. His review in Davis and Blake is less clear on this subject and it appears that he did not have in mind Busse's[3] kinetic theory requirements. There is no reason to believe that his "units" correspond to chain segments or to whole molecules. Terms such as peptizing agents, reversion, retarders, delayed action, depolymerization, chemical softeners, etc., are common in elastomer literature. According to the present review such terms have to do specifically with the scission of links in rubber networks and, in general, with the kinetic theory. In the present section the scission principle is applied to the action of retarders, delayed action accelerators, and certain vulcanizing agents.

Statements are often made in scientific discussion and in suppliers' literature to the effect that retarders, or a certain retarder, retard cure (or scorch) at processing temperatures but do not retard at curing temperatures. Similar statements are frequently made with respect to accelerators, i.e., that a particular accelerator is inactive below some critical temperature and when the critical temperature is exceeded, curing proceeds rapidly. These statements and beliefs were thought by Juve and Shearer[34] to be in error and they conducted work to determine whether or not this was the case. The testing was done with NR black stocks. The base recipe employed was as follows:

Blends of smoked sheets	100
Zinc oxide	5
Carbon black	50
Pine tar	3.5
PBNA	1
Sulfur	3
Stearic acid	1.5

A masterbatch of this composition was prepared and the accelerator and retarder added as needed. For any particular series the same masterbatch was

employed so that the only variable was the accelerator and retarder. Most of the work was done with EPC black but one series was run with FF black. Most of the testing for scorch and cure rate was done with a steam heated Mooney viscometer[35] at various temperatures using the small rotor. In one

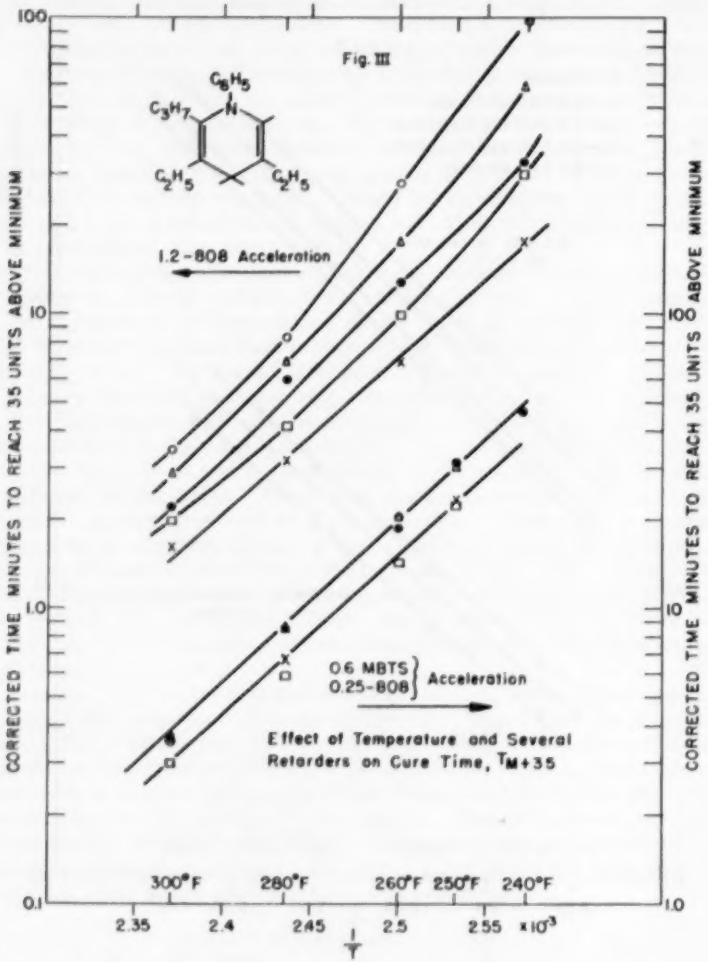


series, stress-strain tests were run at a series of cures at 280° F and hardness and Goodrich flexometer tests run at a single cure of 75′ at 280° F.

In order to determine the dependence of scorching and cure rate on temperature with the Mooney cure test, it was necessary to develop a correction curve for the time lag in heating the Mooney test specimen to the impressed temperature. This was done by preparing heating curves obtained with thermocouples on the ends of the plungers extending into the test specimen and finally

integrating the curing effect which occurred during the heating up period in order to get the value of the correction.

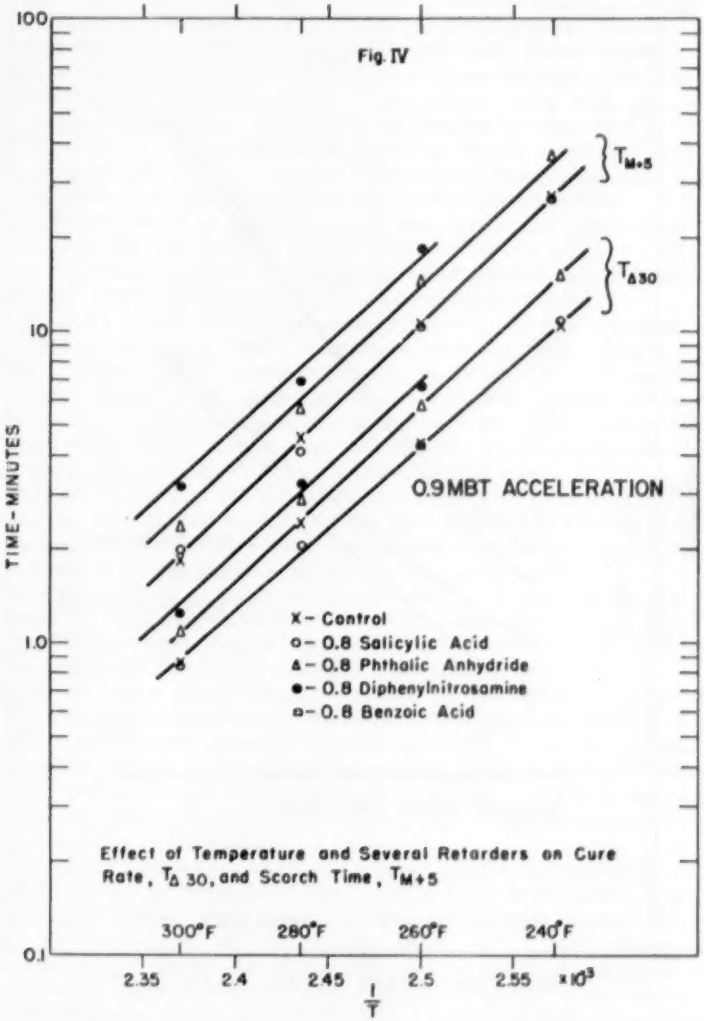
The commercial retarders, Retarder W (salicylic acid), Antiscorch Essen (phthalic anhydride), Vultrol (diphenylnitrosamine), and Retardex (benzoic acid) were tested at various concentrations in stocks with several different ac-



celerating systems all based on NR. Their effectiveness as retarders varies from a slight accelerating effect, to no effect, to varying degrees of retardation, depending on the accelerator used and the concentration of retarder.

In Figures II and III plots are shown of the corrected time to reach T_{M+35} for the various combinations against the reciprocal of the absolute temperature. The quantity, T_{M+35}, is defined as time for the Mooney dial reading to reach

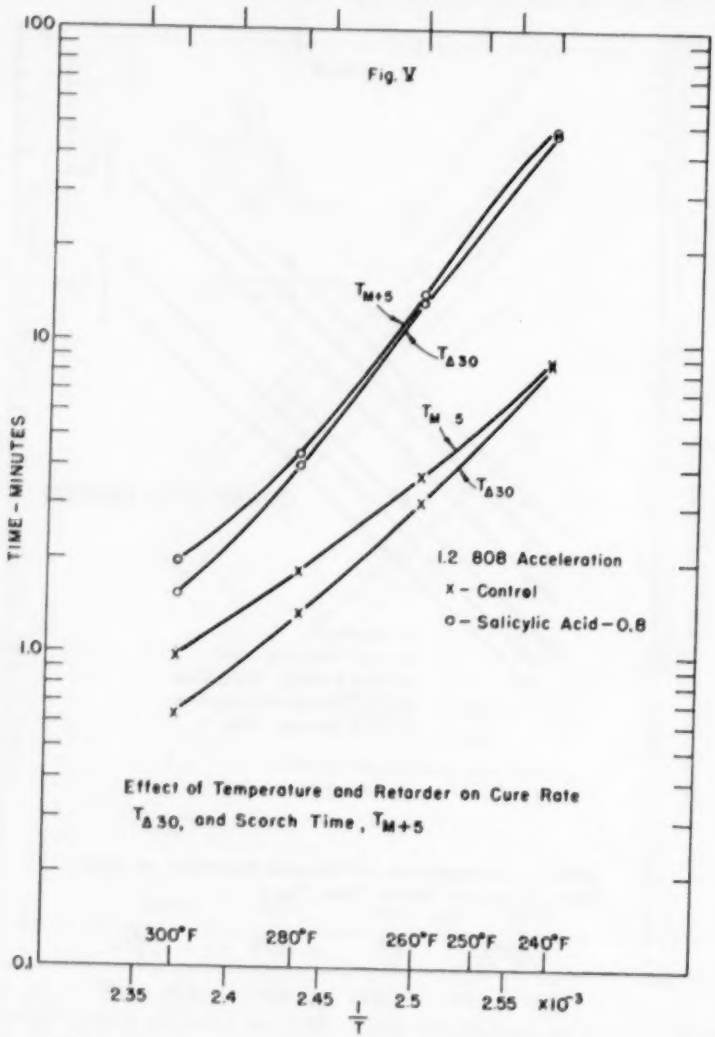
35 units higher than the minimum value and is read as "Mooney cure time at minimum plus 35 units." The difference between T_{M+35} and the scorch time, T_{M+5}, is $T_{\Delta 30}$ and this is an inverse measure of the cure rate. With the exception of the stocks accelerated with Accelerator 808 (sold by the manufacturer as



butyraldehyde-aniline and believed to be a mixture containing N-phenyl-3,5-diethyl-2-propyl-1,4-dihydropyridine as the main active component[36]), all plots were straight lines and all the data for the retarded stocks gave lines parallel to the control. Thus, with these systems any material which retards

does so at all temperatures over the range studied by an amount which is predictable if the degree of retardation at any one temperature is known.

With 808 acceleration the case was somewhat different. The curves for the retarded stocks fan out with respect to the control, particularly at temperatures



below 280° F. This means at 240° F for example, that a stock retarded with salicylic acid is much safer than would be predicted from its behavior at 300° F. However, it should be noted that retardation at 300° F is also appreciable.

The data in Figures II and III are based on the time of heating required to reach a point appreciably beyond the scorch time. It is of interest to deter-

mine whether or not the temperature dependence of the scorch period is the same or different from that of the cure rate.

In Figures IV and V, a portion of the data are plotted, Figure IV for the MBT stock and all four retarders and V for the 808 stock with one retarder. In Figure IV the lines are all essentially parallel showing the same dependence on temperature for the scorch period as well as the cure rate. The two other stocks, i.e., the TMTM stock and the MBTS-808 stock, behave similarly.

None of the retarders behave as they have frequently been reported to behave with respect to temperature, i.e., retard at processing temperatures but not at curing temperatures. With three accelerating systems, MBT, TMTM and MBTS-808, the curves relating the log of the time to scorch or cure to the reciprocal of the absolute temperature were straight lines and parallel to each other, indicating that retardation was uniform at all temperatures. With 808 acceleration the retarders retarded scorch and cure at all temperatures but much more at low than at high temperatures. Thus, according to Juve and Shearer, with this accelerator (which is not widely used today) some real advantage with respect to rate can be gained by using a retarder.

In the MBT system, all four retarders, whether or not they retard, develop higher moduli and higher tensile strength at optimum cure. This is an advantage, of course, but is regardless of rate. It occurred to Juve and Shearer that these materials, in the particular recipe used, may function in the same manner as fatty acids and that diphenylnitrosamine, which was the most effective material in this respect, may also function in a manner similar to the performance of N,*p*-dinitrosodimethylaniline in butyl rubber.

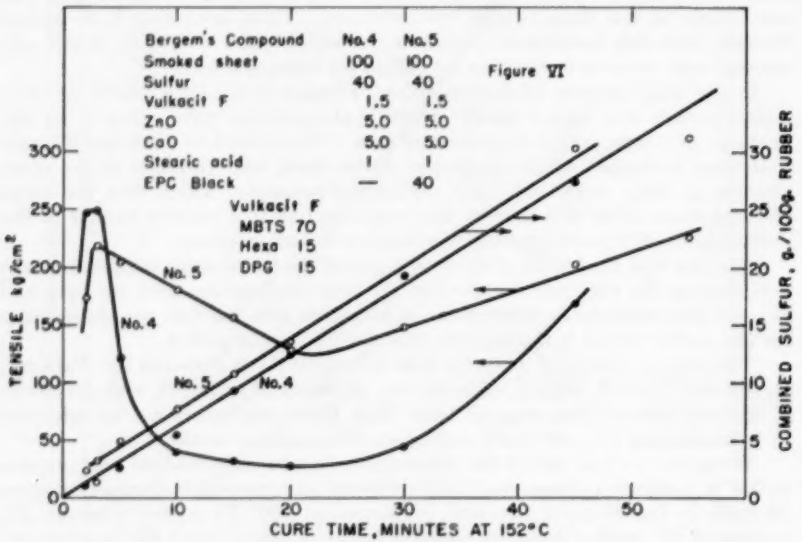
The fact that the length of the scorch period shows the same temperature dependence as the cure rate for three of the four accelerators tried by Juve and Shearer may indicate for these three accelerators that the rate controlling step for the scorch period is the same as that for the curing period.

The various effects of acids on NR, including those depicted by Watson[27], the effects of thiols, oxygen, quinone, etc. as chemical softeners, and the effects of diphenylnitrosamine, suggest that when these substances act as retarders of vulcanization they are really acting as chain scission agents.

When one to four phr of the nitrosamine in acetone-extracted pale crepe is milled in a nitrogen atmosphere for two hours, an appreciable decrease of some 10 units in the Mooney viscosity (measured at 260° F) occurs, whereas, the milling of the rubber alone in nitrogen causes a pronounced rise in viscosity. The rise noted for nitrogen milling in the range of 120° F to 160° F can amount to 40 Mooney units and is explained by the radical mechanism discussed above, the rise being due to crosslinking.

Although the nitrosamine was a mild scission reagent during nitrogen milling at a relatively low temperature, it was found to be a potent chemical softener in the press at 260° F. This scission activity accounts for its usual retarding effect. Nevertheless, at this temperature it can also have a curing effect. Amine-free rubber, lightly cured, was obtained by distilling a mixture of extracted natural rubber and 4 phr of the nitrosamine at 130° C and 0.01 mm in the shortpath still. A gas, presumably NO, was evolved while diphenylamine and unreacted diphenylnitrosamine were collected as distillate. Other evidence of curing was that in the Mooney test described above for the nitrosamine-containing rubber, it was found that the dial reading rose slightly during the 15 minutes of running. Barton[27] reported diphenylnitrosamine (5.0 phr) as a replacement for ZnO in the base recipe: sulfur 0.64 phr, ZnDMDC 2.0 phr, and dibenzylamine 1.5 phr. This is a curing effect.

It has been considered that diphenylnitrosamine[38] is a convenient source of pure NO and even an *in situ* source of this reagent for detecting hydrocarbon radicals. Rowe and Diller[39] found by mass spectrometer techniques that NO is the only gas evolved when the nitrosamine is warmed to 100° C. When rubber was allowed to stand in a 60–40 nitric oxide-nitrogen mixture for four days at 25° and the gas analyzed it was found that the gas had changed to a concentration of about 50 per cent nitric oxide. The rubber was soluble in benzene with no apparent degradation or crosslinking. The amount of NO reacting with the rubber was very small. However, when rubber is milled in an NO atmosphere degradation is pronounced, NO being about equivalent to oxygen as a scission reagent. Apparently the radical ends formed by mechanical breakage of the rubber chains react readily with NO. The reaction of NO with isobutene has recently been reported on by J. F. Brown[40] who believes there is



no reaction except that initiated by traces of NO_2. Our observation of slight reaction of NO with rubber at rest could well be due to a similar initiation by NO_2 fortuitously present. Bloomfield and Jeffrey[101] reported NO to react during 30 to 120 minutes with 5 grams of NR in 300 ml of carbon tetrachloride.

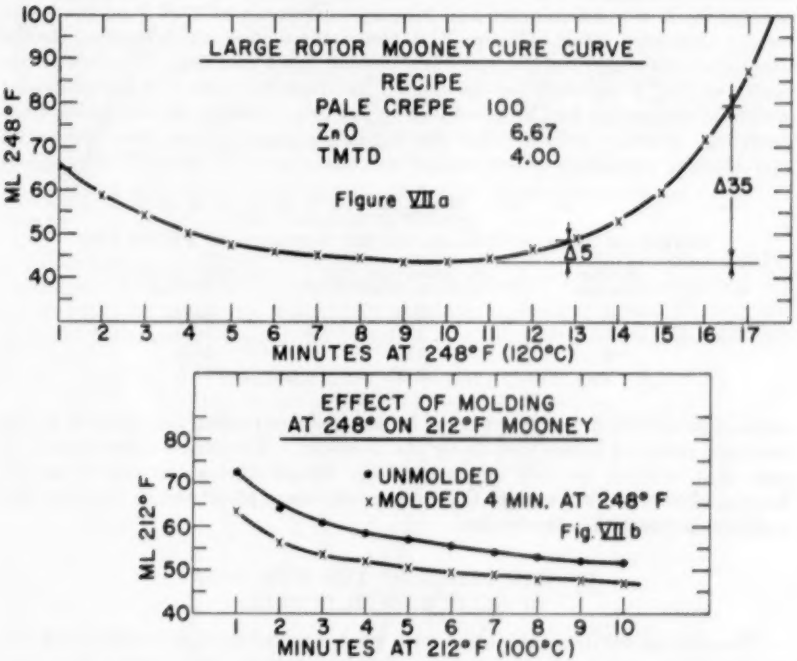
Phthalic anhydride has a mild chemical softening action on NR during milling in nitrogen at 50–70° C as compared to diphenylnitrosamine. Yet the temperature dependence of the rates of these retarders for both the scorch period and the cure period are the same. This leads to the idea that some unit of the rubber chain is involved which can either cleave or crosslink. And further, if this is true, the scission reaction should be first order (as actually found by Watson for acid initiated degradation and by several workers for the stress relaxation of vulcanizates) and the crosslinking reaction should be second order.

Among the effects of phthalic anhydride, benzoic acid, salicylic acid or diphenylnitrosamine on NR, it seems important that at curing temperature, e.g.,

260° F in the press, all are, or may be, rather potent chemical softeners. Presumably, except for the nitrosamine, the effects are by way of ionic scission, but there is always the possibility that the protonated isoprene units may prefer to cleave by a radical mechanism as well as to crosslink through a radical intermediate which is also common to the cleavage reaction.

It is believed that the mild crosslinking effect and the evolution of diphenylamine observed with diphenylnitrosamine are related but these actions need further study.

Rubber at ordinary temperatures seems stable enough, as pointed out by Farmer[41]. However, when heated with a large amount of sulfur in the preparation of hard rubber it is seen to pass through various stages. The tensile



and the elongation drop precipitously after a few per cent of sulfur have combined which is shown by the data of Bergem[42] for accelerated hard rubber stocks. These data are plotted in Figure VI. The degradation in the early stages of the hard rubber cure has been called depolymerization (see, for example, Numajiri[43]). Degradation or, at least, a change associated with low tensile and low elongation remains predominant until about twenty per cent of sulfur has combined. Polymerization then sets in as shown by the rather rapid rise in tensile. The early stages may be considered as the hard rubber scorch period. The hard rubber cure will be considered again in other sections.

Vulcanizing agents other than sulfur can exhibit chemical softening. For example, *tert*-butyl peroxide[44] and decamethylene dis-methyl azodicarboxylate[45] are sometimes referred to as quantitative crosslinking reagents in the sense that

the numbers of crosslinks introduced per unit quantity of vulcanizate may be related quantitatively to postulated chemical reactions. However, the scission effects of these reagents are so potent that in butyl, which has a low concentration of crosslinking sites, the overall effect is one of chemical softening. This scorch period scission action seems to be a general property of curing agents. Even sulfur chloride, S_2Cl_2, is seen to act as a scission agent for natural rubber if the concentration is sufficiently low (see the next section). A test for possible scission activity of TMTD showed that this often potent curing agent was no exception. The recipe (TMTD 4.00) contained pale crepe 100, ZnO 6.67 and TMTD 4.00. Stock was purposely mixed to a rather high viscosity and gave the Mooney curve cure shown in Figure VIIa. The scorch time, T_{M+5}, is seen to be 13.7 minutes at 248° F. Samples (25 g) were molded for 2, 4 and 6 minutes and Mooney curves run at 212° F on these and on the unmolded stock. Figure VIIb shows the curves which resulted for the unmolded stock and for the specimen molded for 4 minutes. The lower viscosity at 212° F observed for the molded specimen indicates that the molecular weight of the rubber had been reduced by heating 4 minutes at the curing temperature. Further evidence for this reduction were the inherent viscosities and Mooney viscosities of the molded specimens given in Table I. The specimens were soluble in benzene except for the zinc containing components which were not removed before measuring the viscosity. These and other data indicate that scission, as well as crosslinking, occurs during the scorch period. Rate studies of sulfur combination and crosslinking, presented in the next two sections, support this conclusion.

TABLE I

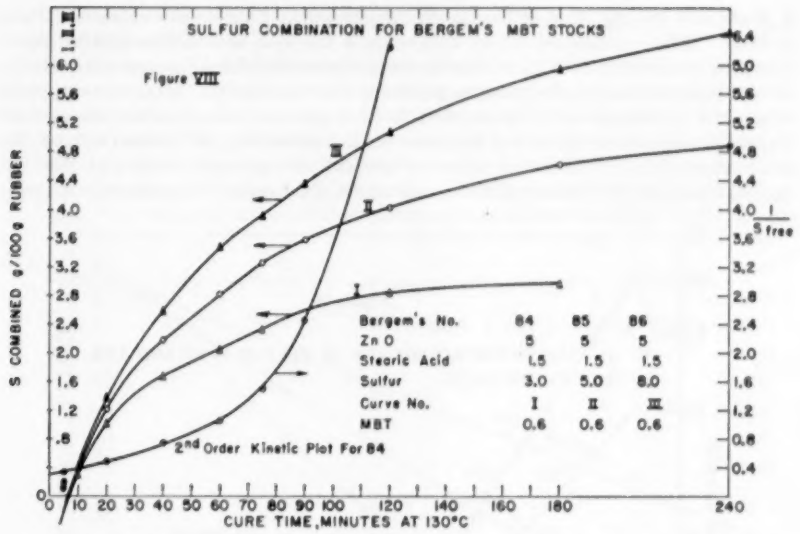
EFFECT OF TIME OF MOLDING ON THE VISCOSITY OF TMTD 4.00

Molding time min	Inherent viscosity, $[\eta]_0$ in benzene at 25° C	Mooney viscosity 212° F-ML-1′
0	3.12	64.0
2	2.93	59.0
4	2.87	56.0
6	2.92	57.5

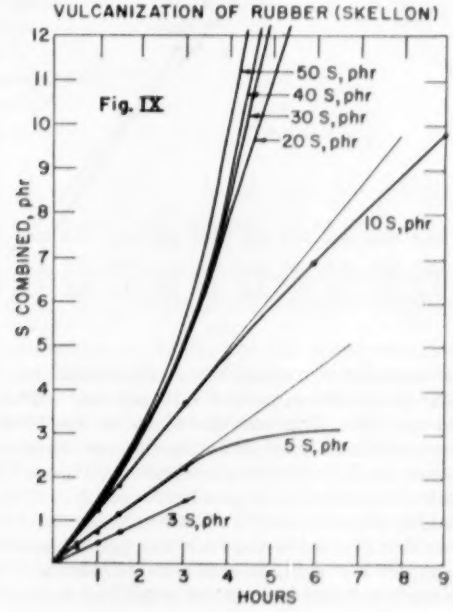
IV. THE ORDER OF THE REACTION OF SULFUR WITH RUBBER

The rate of sulfur combination with rubber under various conditions needs study with respect to the three stages of vulcanization. It is known that total combined sulfur is not a good general criterion for state of cure, but it is widely felt that an accurate knowledge of the rates of formation of the various types of combined sulfur would help in the understanding and use of the vulcanization process. It is often stated that the rate of combination for accelerated soft rubber stocks is proportional to the concentration of free sulfur, i.e., it is first order in sulfur concentration.

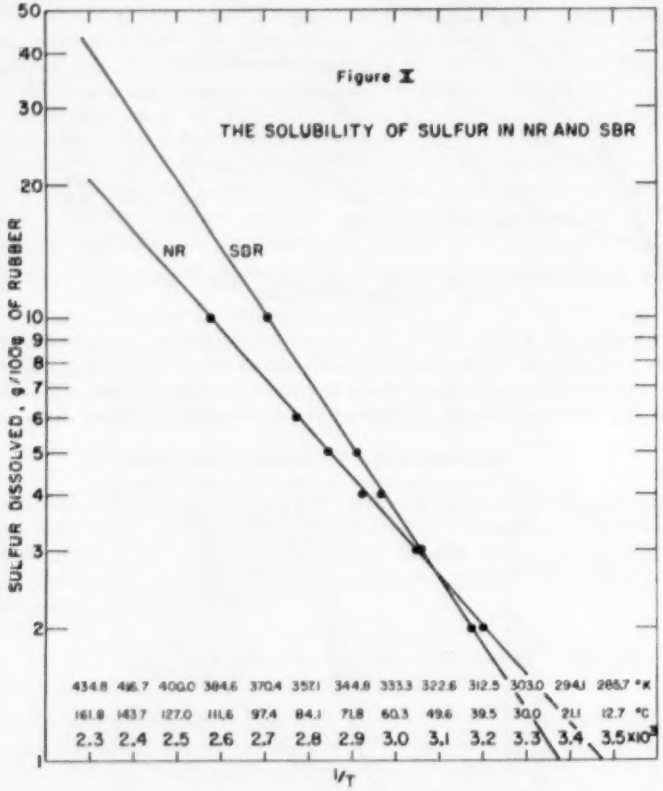
Actually sulfur combination may not be accurately first order, or even pseudo unimolecular. Thus in Figure VIII are plotted Bergem's[46] data for the variation of sulfur in three recipes, one being fairly close to the ACS 1 formulation. The curves all show flat segments, i.e., linear intervals where the rate of reaction is independent of time and, therefore, of free sulfur concentration for any particular initial concentration of sulfur.


SULFUR COMBINATION FOR BERGEM'S MBT STOCKS
Figure VIII
S COMBINED g/100g RUBBER
1/S free
CURE TIME, MINUTES AT 130°C
Bergem's No. 84 85 86
Zn O 5 5 5
Stearic Acid 1.5 1.5 1.5
Sulfur 3.0 5.0 8.0
Curve No. I II III
MBT 0.6 0.6 0.6
2nd Order Kinetic Plot For 84

The curves in Figure VIII also reveal an induction period of about five minutes. Thus, the point made recently by Veith[47] that vulcanization rate curves may be of sigmoid shape has a considerable basis in fact. Nordlander[48] studied the data previously published for rubber-sulfur mixes, e.g., those of

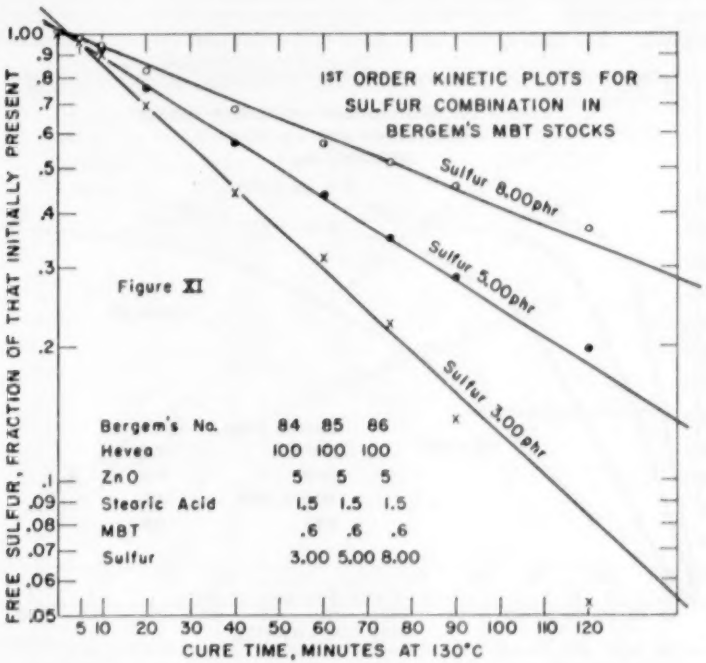


Spence and Young[49] and of Skellon[50]. Spence and Young used extracted Para rubber. Their combined sulfur values show the rate of reaction at 135° for a mixture containing 37.41% sulfur to remain constant for 16 hours until nearly 30 per cent sulfur (on the reaction product) had combined. Reactions stopped when the combined sulfur amounted to 32.0 per cent which is the theoretical value for one sulfur atom per isoprene unit. According to Skellon's data, for concentrations of 10 per cent sulfur or less the rate of combination at 140° remains constant for two or three hours and then begins to decrease. The reaction thus, is only initially zero order. For concentrations above 10 per cent, the rate is initially about the same as for 10 per cent sulfur, but after about an hour, increases rapidly. This was stated to be due to an increase in the solubility of sulfur as the combined sulfur in the vulcanizate increases. Skellon's data as graphed by Nordlander, are shown in Figure IX. The effect of temperature on sulfur solubility is shown by Figure X. The data plotted are those of Kemp, Malm, and Stiratelli[51]. Extrapolation to 140° gives a value of 15 g per 100 g of rubber instead of the 10.2 phr value found by Skellon. This value, probably on the low side, is considerably above 10 per cent and so Nordlander's explanation of an increase of solubility to account for Skellon's



rate values for mixes containing more than 10 per cent sulfur for the moment does not seem plausible.

For mixes containing 10 weight per cent sulfur or less, Nordlander related the rate of vulcanization at various temperatures to the concentration at the same temperature of μ (insoluble) sulfur in liquid sulfur. At 140° it amounted to one per cent. The insoluble sulfur concentrations were those determined by Aten[52]. In order to account for the temperature coefficient of combination Nordlander considered that only a fraction of the μ sulfur had sufficient energy to react. In the end, he concluded adsorption of sulfur to rubber to be the ex-

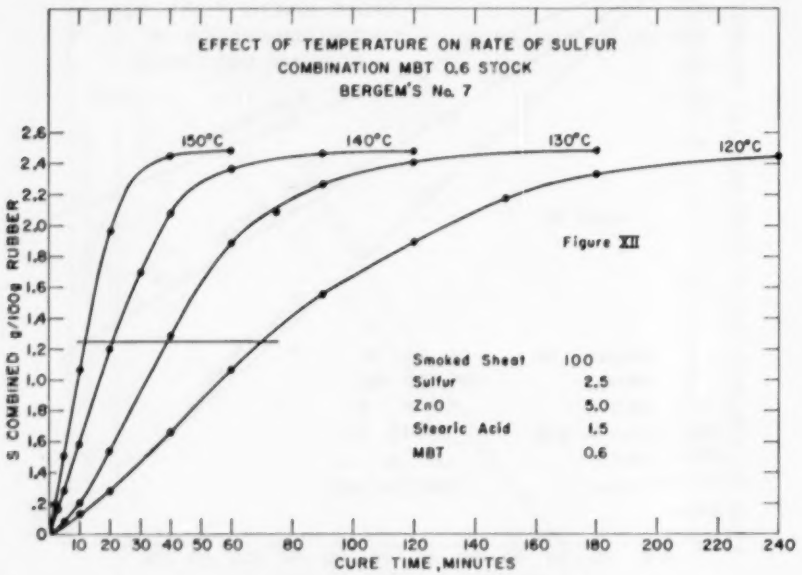


planation for the zero order character of the reaction for any initial concentration and, at the same time, the fact that the constant rate does increase with the initial concentration.

Nordlander's views are of value, but the adsorption feature is obviously weak. A realistic suggestion is that of Bergem[53], namely, that sulfur combination facilitates further reaction. The data collected by Williams[54] and confirmed by Bergem[55] that mild degradation of vulcanizates followed by fractionation provided both sulfur-rich and sulfur-poor fractions support this view as do the recent findings of Bateman and coworkers[25] that additional sulfur atoms tend to be located near sulfur-containing crosslinks. There are various reasons to believe that crosslinks may make adjacent segments of the main chains more reactive so that subsequent reactions should fix sulfur atoms, perhaps as additional crosslinks, near the original crosslinks. In this way the functionality of linking could increase. Bergem's explanation of increasing activity with

increasing vulcanization presumably should apply to high sulfur recipes as well as to low. Thus, it is not *necessary* to invoke an increase in sulfur solubility to explain the increase in reaction rate with time that has been observed for high sulfur mixes. Increase in solubility may be, and probably is, a contributing factor, however. It seems clear that Bergem's explanation applies with certainty to mixes containing less than about 10 per cent sulfur.

Evidence that solubility is an important factor in the reaction of sulfur with rubber is in the results of Whitby and Jane[56]. These authors found that 5 per cent solutions of pale crepe in dichlorobenzene were very reactive at 140° with a tenfold excess of sulfur (320 g sulfur per 68 g rubber) both reactants dissolving completely. The combined sulfur approached 32 per cent at long times of heating. The data gave a fairly good first order plot (not shown) calculated

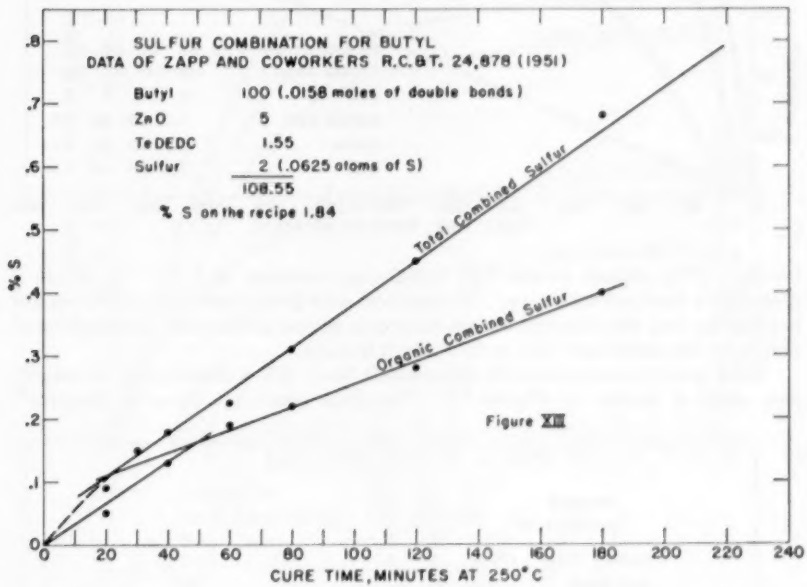


on the basis that 32 per cent combined sulfur is equivalent to 100 per cent reaction. From this the half life can be estimated as about eighty minutes. As shown by Figure IX, up to 80 minutes of reaction for Skellon's mixtures initially containing more than 10 per cent sulfur, the combined sulfur amounted to less than 2 per cent. This is low compared to 16 per cent in the work of Whitby and Jane. However, if the combined sulfur values of these investigators at one and two hours reaction time are divided by ten, the resulting values fall on Skellon's plot.

We thus conclude, with Nordlander, that solubility for high sulfur mixes is rate controlling. And, further, since in Whitby and Jane's work the sulfur was present in tenfold excess and the data gave a first order plot, it is likely that the rate is first order in C_8H_8 units.

Accelerated low sulfur stocks containing zinc oxide seem prone to react according to the first order law as far as sulfur combination is concerned. The first order plots corresponding to the rate curves of Figure VIII constitute

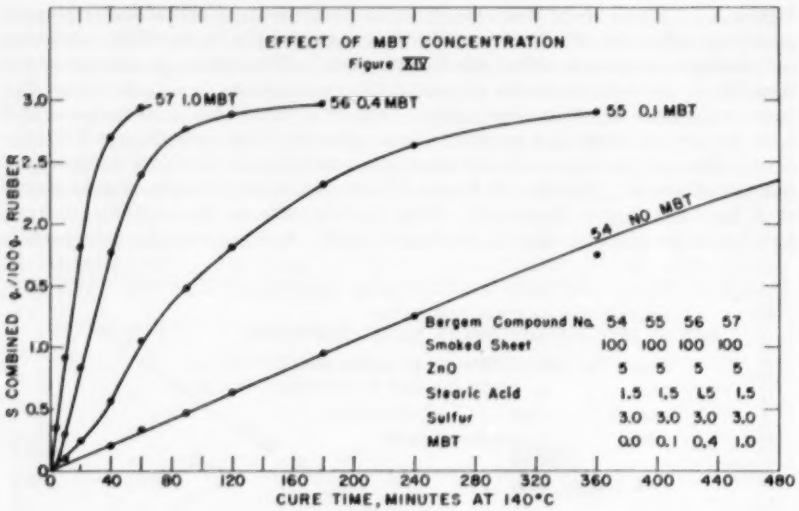
Figure XI. These show that even the stock containing 8 phr of sulfur gives a good first order plot, the time periods of constant rate in Figure VIII not being sufficiently extensive to affect the kinetic plots. The sulfur concentration for these plots, in order to make them directly comparable, is calculated on the basis of the ratio of free to total sulfur. Since the first order plots are good and since the second order plot for the 3 phr of sulfur stock given in Figure VIII is a curve with a high degree of curvature, the consumption of sulfur evidently is not second order. The lines in Figure XI are seen to cut the zero-time ordinate at a fraction greater than 1.00. This merely reflects the induction period noted also for the rate curves in Figure VIII. As suggested by Auerbach[57],



MBT-ZnO compounds may have an induction period due to the time required for the zinc salt of MBT (the "real" accelerator) to form, but, no doubt, other factors may also contribute to the induction period.

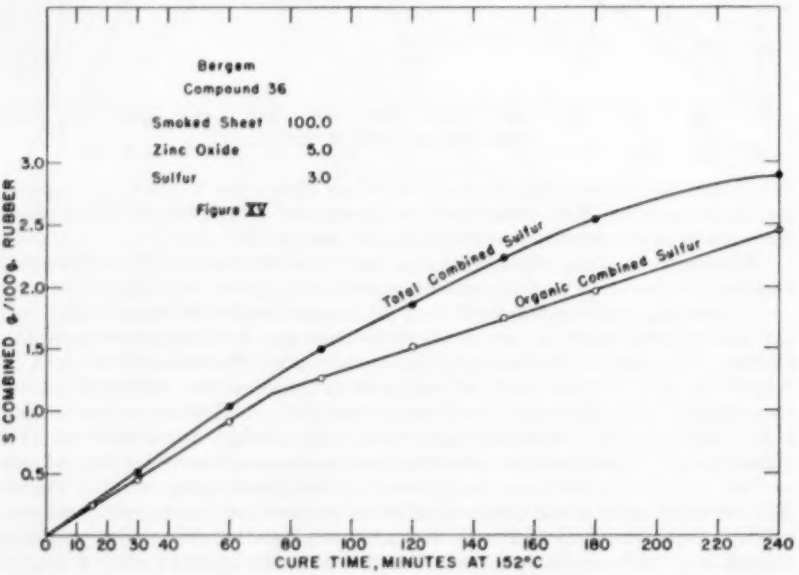
When a fairly high temperature, e.g., 140° C, is used with MBT-ZnO stocks, combined sulfur data may not reveal an induction period (see Figure XII).

It was suggested by Gordon[58] that sulfur combination in butyl (IIR) vulcanization is first order as the result of the slow step being the opening of the S_8 ring. This cannot be the case, however, for the different rubbers, such as NR, SBR, and IIR then would all vulcanize at the same rate, which, of course, they do not. NR vulcanizes much faster than SBR and SBR much faster than IIR. Actually, the combined sulfur data of Zapp and coworkers[59] for IIR vulcanization, which had been used by Gordon, show a zero order dependence on free sulfur concentration during most of the crosslinking period. Figure XIII includes plots of the total combined sulfur and also the organic combined sulfur. Less than half of the sulfur combines, but then the recipe contains almost four times as many gram atoms of sulfur as it does moles of double


EFFECT OF MBT CONCENTRATION
Figure XIV
57 1.0 MBT
56 0.4 MBT
55 0.1 MBT
54 NO MBT
Bergem Compound No. 54 55 56 57
Smoked Sheet 100 100 100 100
ZnO 5 5 5 5
Stearic Acid 1.5 1.5 1.5 1.5
Sulfur 3.0 3.0 3.0 3.0
MBT 0.0 0.1 0.4 1.0
S COMBINED g./100g. RUBBER
CURE TIME, MINUTES AT 140°C

bonds. With respect to the high initial concentration of sulfur the recipe is more like a hard rubber recipe. No analyses were given for short cure times but it could be that the reaction has an induction period as does the crosslinking of IIR to be discussed later and as do many NR cures.

That sulfur combination in accelerated hard NR vulcanization is largely zero order is shown by Figure VI. The data again are those of Bergem[42].



Combined sulfur-cure time plots are included for a loaded and an unloaded stock. For the loaded stock the line is appreciably above the origin. Thus, for the latter case, as for the cure data for IIR in Figure XIII, there is a sharp rise in sulfur combination just before linear behavior sets in. Here again it may be presumed that there is an induction period just prior to the sharp rise.

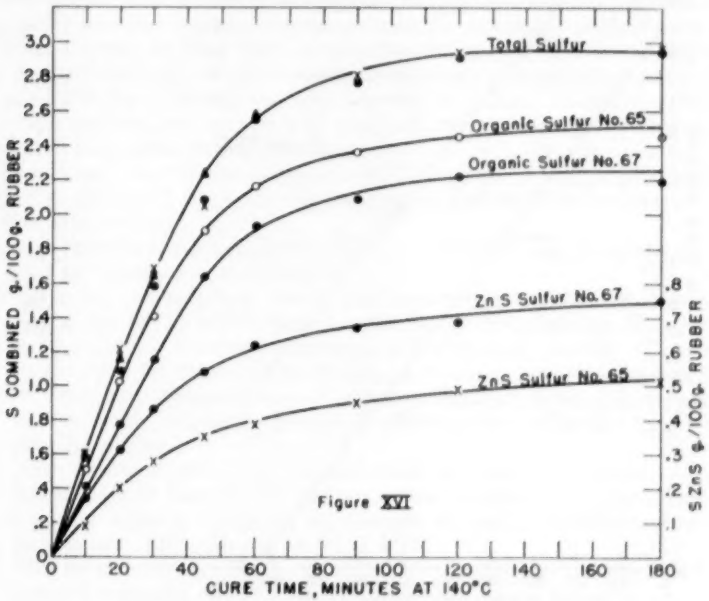


Figure XVI

Bergem No.	65	66	67
First Latex Crepe	100	100	100
Sulfur	3	3	3
ZnO	5	5	5
MBT	0.6	0.6	0.6
Stearic Acid	0	0.5	3
PLOT POINTS			
Total Combined S	x	▲	●
Organic S	o		●
ZnS S	x		●

The rate of combination of sulfur with NR in the presence of zinc oxide and fatty acid, as is well known, is strongly increased by MBT. Bergem's data[60] on this are shown in Figure XIV. It should be kept in mind that the rate for the recipe without MBT would have been much slower had extracted NR been used.

The presence of zinc oxide in a 3 phr sulfur-NR mix has little effect on the rate of sulfur combination. Figure XV is a plot of Bergem's data[61] for total and organic combined sulfur for 3 phr of sulfur and 5 phr of zinc oxide at 152° C. His data for the 3 phr sulfur (no zinc oxide) recipe show a slight induction period but otherwise fall very near the curve in Figure XV for total combined sulfur. The first order kinetic plot for the total combined sulfur data of

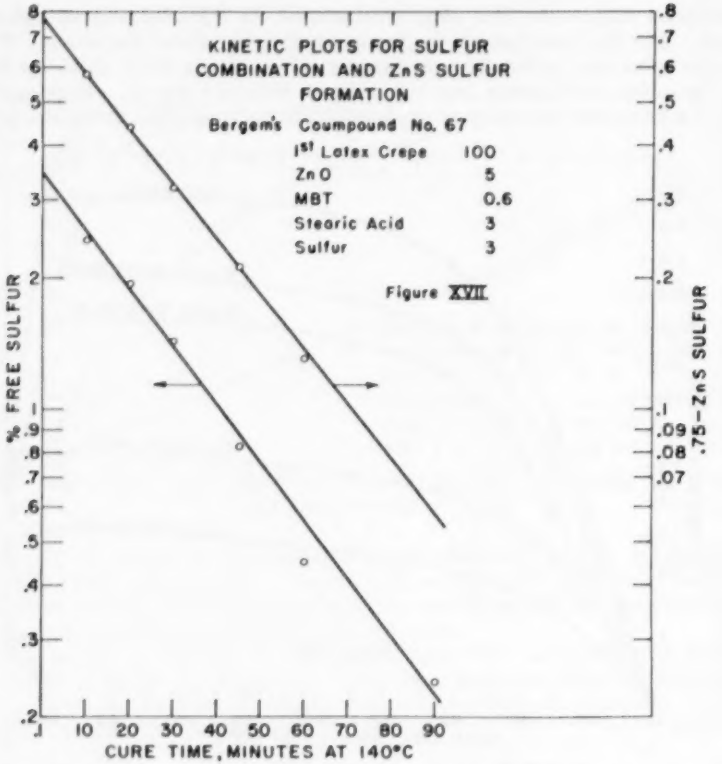


Figure XV was not quite linear, the deviation being in favor of a zero order plot. It will be noted that the organic combined sulfur values in Figure XV fall on one or the other of two intersecting lines and that the line for the short cure times passes through the origin. There was no induction period.

TABLE II

	Compound 65		Compound 66		Compound 67	
Latex crepe	100		100		100	
S	3		3		3	
ZnO	5		5		5	
MBT	0.6		0.6		0.6	
Stearic acid	0		0.5		3.0	
Cure time in minutes at 140° C	Total combined sulfur g/100 g rubber	Sulfide sulfur g/100 g rubber	Total combined sulfur g/100 g rubber	Sulfide sulfur g/100 g rubber	Total combined sulfur g/100 g rubber	Sulfide sulfur g/100 g rubber
10	0.60	0.09	0.61	0.14	0.58	0.17
20	1.21	0.20	1.16	0.28	1.08	0.31
30	1.68	0.28	1.65	0.36	1.58	0.43
45	2.24	0.35	2.24	0.48	2.18	0.54
60	2.55	0.39	2.58	0.55	2.55	0.62
90	2.81	0.45	2.80	0.63	2.76	0.67
120	2.94	0.49	2.94	0.67	2.91	0.69
180	2.96	0.51	2.95	0.69	2.94	0.75

The effect of stearic acid in vulcanizations accelerated with mercapto thiazoles has traditionally been to enhance the effect of zinc oxide. The data[62] of Table II and the data of Figures XVI and XVII show in what way the formation of ZnS sulfur is affected. It definitely is increased by stearic acid but the rate of total sulfur combination is not. The kinetic plots in Figure XVII have the same slope. This behavior is in agreement with the assumption that zinc oxide, in the presence or absence of stearic acid, for any single mixture converts a constant fraction of the combined sulfur to ZnS sulfur. No doubt this is a factor to be considered in the evaluation of Zapp's organic combined sulfur data of Figure XIII since in the determination of organic combined sulfur in butyl he heated swollen samples with oleic acid in order to remove zinc oxide. Zinc sulfide is not removed by hot oleic acid.

In summary, the reaction of sulfur with NR in soft as well as hard rubber recipes has displayed the following important features with respect to rate of sulfur combination:

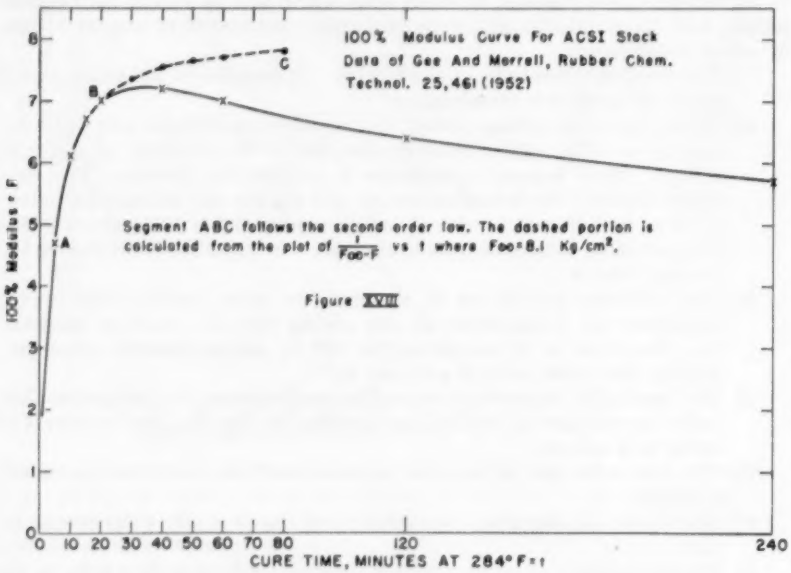
1) The reaction tends to be autocatalytic. It displays an induction period at a sufficiently low temperature.
2) Following the induction period, the reaction tends to be zero order for any given initial sulfur concentration below the solubility of sulfur in rubber. Such behavior constitues a self-limiting feature. The best explanation for the induction period, and for the rate being independent of time, and therefore, also of sulfur concentration for a given initial concentration, is that the product is more reactive with sulfur than is the starting rubber.
3) The induction period can be shortened or made undetectable by (a) increasing the temperature or (b) adding suitable auxiliary reagents, e.g., zinc oxide or (c) increasing the rate by adding suitable concentrations of zinc oxide, stearic acid and MBT.
4) The zero order dependence on sulfur concentration is changed to first order dependence on rubber concentration by use of a tenfold excess of sulfur in a solvent.
5) The zero order rate of reaction increases with the initial concentration of sulfur.
6) Zinc oxide, or, zinc oxide plus stearic acid does not affect the zero order rate.
7) The combination of sulfur with NR strongly tends to be first order in the presence of zinc oxide, fatty acid, and accelerator and shows an induction period if the rate is sufficiently low.
8) The rate limiting step in sulfur combination during vulcanization involves participation of the rubber and any accelerating system that may be present such as MBT-ZnO-fatty acid.

The combination of sulfur is zero order in the vulcanization of IIR in the presence of zinc oxide, fatty acid, and accelerator. Here the reaction is autocatalytic even for the low concentration of double bonds of the IIR. And, of course, the reaction is slow as compared to that with NR.

V. THE ORDER OF RUBBER CROSSLINKING REACTIONS AND THE POSSIBILITY OF CHAIN SCISSION

Previous reviews[54,62] have usually pointed out that state of cure is not proportional to total combined sulfur or even to organic combined sulfur. Some workers have said that state of cure, at least under certain conditions, can be

gaged by zinc sulfide[64] formation, others that zinc sulfide content is a measure of reversion[65] (crosslink or main chain scission), and still others consider the zinc atom to be an integral part of the crosslink in which it functions as a connection between two sulfur atoms which in turn are attached to different rubber chains[66]. Elastomers containing controlled concentrations of carboxyl groups have been prepared in recent years and rather extensively studied. Several are in commercial production. Their zinc salts often are "vulcanizates" containing the zinc salt crosslink as the structural feature leading to stiffening and they have properties quite different from those of the usual vulcanizates. It thus seems improbable that such crosslinks make any important contribution to the state of cure in ordinary NR vulcanization. This follows in part because the concentration of carboxyl groups[75] in NR is known to be small and



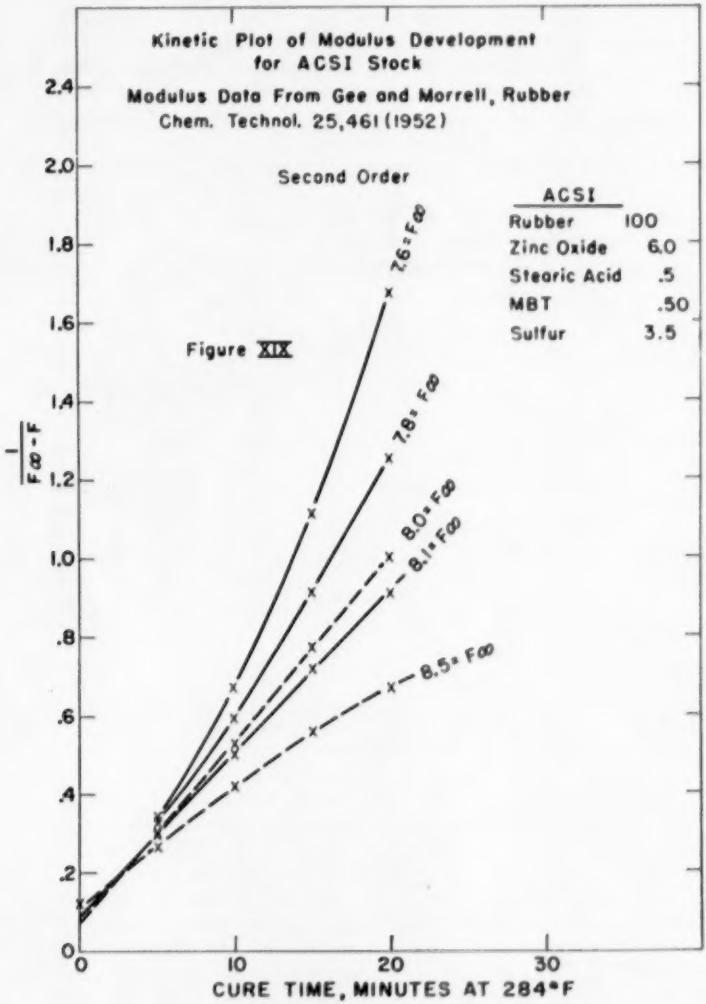
to be located frequently at chain ends (compare Section VIa). Polymers vulcanizable through zinc salt formation are dealt with by H. P. Brown in the following Rubber Review entitled, "Carboxylic Elastomers".

If, in general, our most useful rubbery networks are formed with sulfur in the presence of zinc oxide, which is believed to be true, then an important problem exists to account for the indefinite amount of sulfur that is needed to effect crosslinking as well as for the absence of zinc in the crosslinks. Rate studies here aim to serve as adjuncts to other approaches.

Sulfur combination is first or zero order depending on conditions, usually following an induction period in which chain scission occurs. Sulfur combination rates were discussed in the previous section. The present section considers the order of the crosslinking step and also the concurrent scission reaction.

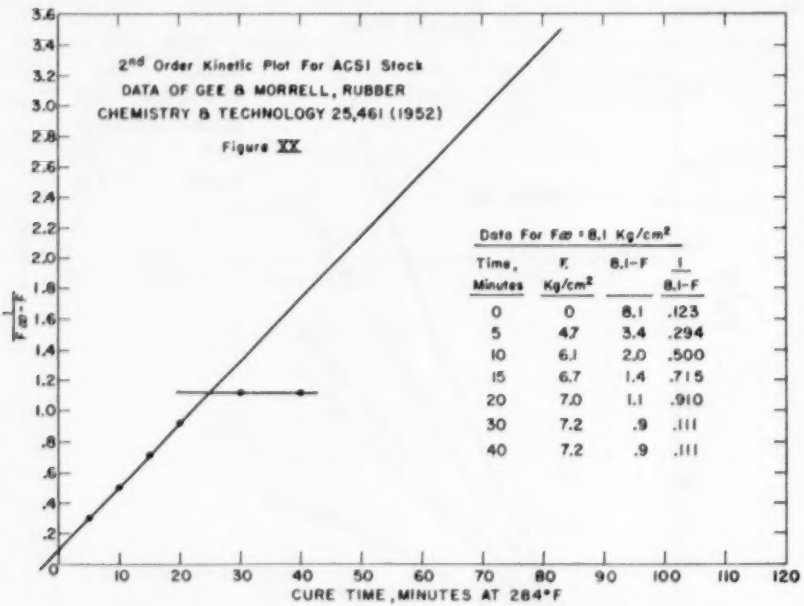
It was reported by Gee and Morrell[68] that the crosslinking reaction, which they followed by measurement of 100 per cent modulus, was about three times as fast as the sulfur combining reaction at 140° C for the ACS 1 recipe. They

stated rates as first order constants and allowed for initial modulus before vulcanization and for reversion. Figure XVIII is Gee and Morrell's modulus curve up to 240 minutes of cure. After 20 minutes, reversion is more noticeable. Understandably the very early part of the cure period also is uncertain.



By the conventional method of estimating reversion it may be noticed from Figure XVIII that the modulus drop is from 7.2 at 30 minutes to 5.7 kg/cm^2 at 240 minutes of cure. This drop is due to network degradation and is commonly ascribed to crosslink scission. The view taken here is that it may also be due to primary chain scission and that two other important types of network

reaction may occur. These are segment interchange and endlinking both of which may lead to the entry of sulfur into the main chain segments. By main chain segments is meant those which are elastically active. The possibility that sulfur atoms in such segments may contribute kinetically was pointed out to the author by D. L. Loughborough[69]. Such activity should be less intense than the activity of segments composed only of carbon and hydrogen. In any case, the mechanism by which the network is formed, the functionality of crosslinks reduced (a form of reversion), and other structural features rearranged, is reserved for later discussion. Here we are concerned with the overall order of initial crosslinking.


2nd Order Kinetic Plot For ACSI Stock
DATA OF GEE & MORRELL, RUBBER CHEMISTRY & TECHNOLOGY 25,461 (1952)
Figure XX
Data For F∞ = 8.1 Kg/cm²
Time, Minutes | F, Kg/cm² | 8.1-F | 1/(8.1-F)
0 | 0 | 8.1 | .123
5 | 4.7 | 3.4 | .294
10 | 6.1 | 2.0 | .500
15 | 6.7 | 1.4 | .715
20 | 7.0 | 1.1 | .910
30 | 7.2 | .9 | .111
40 | 7.2 | .9 | .111
1/(8.1-F)
CURE TIME, MINUTES AT 284°F

For the present then, the main effect in the formation of a network from an all linear system of molecules may be considered to be the formation of tetrafunctional crosslinks. A simplified but ample scheme is that, first, active sites are produced by a relatively rapid process along the chains. These sites next may do one of at least two things. One involves scission, the other crosslinking, and both may involve sulfur. The involvement of sulfur is immaterial at the moment. In agreement with Watson, it is assumed that the scission reaction is first order[27]. This makes it important in the early and in the late stages of curing since it can occur at low concentrations at which the second order process of dimerization of active sites cannot. This second order nature of crosslinking and first order nature of scission, though not properly cointerpreted, have been known of for a long time. For example, Garvey[67] found that dilute (1.0 per cent) rubber solutions in the presence of sufficiently low (1.0 per cent) concentrations of S_2Cl_2 became less viscous when they stood a few minutes. The viscosity then rose sharply during 2.5 hours and during the final 2.5 hours

declined to a value less than the original viscosity. It is reasonable to assume that the decrease in viscosity during the early and late periods is due to chain scission and that the intermediate increase is due to crosslinking.

Returning now to Figure XVIII, the modulus values (F) at 4, 10, 15, and 20 minutes of cure may be scaled off. Using these and various assumed F_∞ values it can be found when $F_\infty = 8.1$ kg/cm^2 that a good second order kinetic plot, Figure XIX, is obtained. This figure shows plots for some other values of F_∞ that are not satisfactory. Figure XX is the second order plot for $F_\infty = 8.1$ kg/cm^2 extrapolated to 80 minutes. It may be noted that the line does not pass through the 0 time value of $1/(F_\infty - F)$, this value being 2 minutes off the line. We may consider this as the scorch period.

Various kinds of evidence for this approach to vulcanization can be found. The preceding section on chain scission during the scorch period dealt at some length with delayed action on this basis and the drop in viscosity of dilute NR solutions produced by concentrations of S_2Cl_2 below one per cent on the rubber definitely supports it. Berkowitch, Charlesby, and Desreux[70] recently reported that all polymers, even those which normally crosslink, undergo degradation when subjected to high energy radiation at low concentration. The useful but relatively mild vulcanizing agents such as cumyl peroxide vulcanize the high unsaturation polymers, NR and SBR, but fail to cure IIR. Apparently, the active sites in IIR undergo scission (a first order change) before their concentration is high enough to undergo the second order dimerization which is crosslinking. Some important evidence involves work by Martin, Roth and Stiehler[71] on stress-strain measurements and that of several groups on swelling measurements for following cure rates.

Martin, Roth, and Stiehler[71] recently reported on the rate of cure of a stock composed of:

MBT 1.00

Natural rubber	100.0
Zinc oxide	5.0
Sulfur	2.50
Mercaptobenzothiazole	1.00
Stearic acid	1.00
Phenyl-2-naphthylamine	1.00

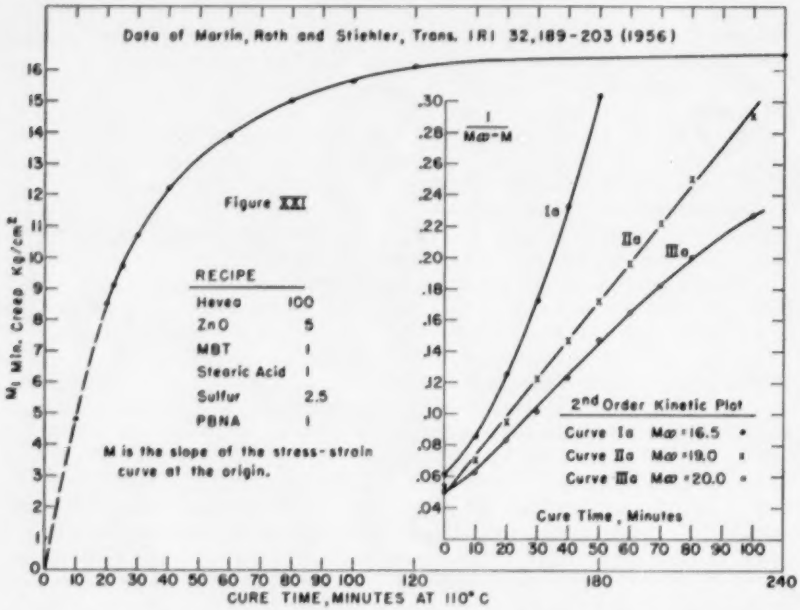
This stock, hereafter known as MBT 1.00, was cured for various periods at 110° C.

The stress-strain relationship was used for following the development of cure. Full allowance was made for the occurrence of creep so that the modulus, M, the slope of the stress-strain curve at the origin, could be computed and used as the measure of state of cure. Actually, up to about 200 per cent extension, the following equation was used for computing M where F is the stress (kg/cm^2), L is the extension ratio, and A is a nearly

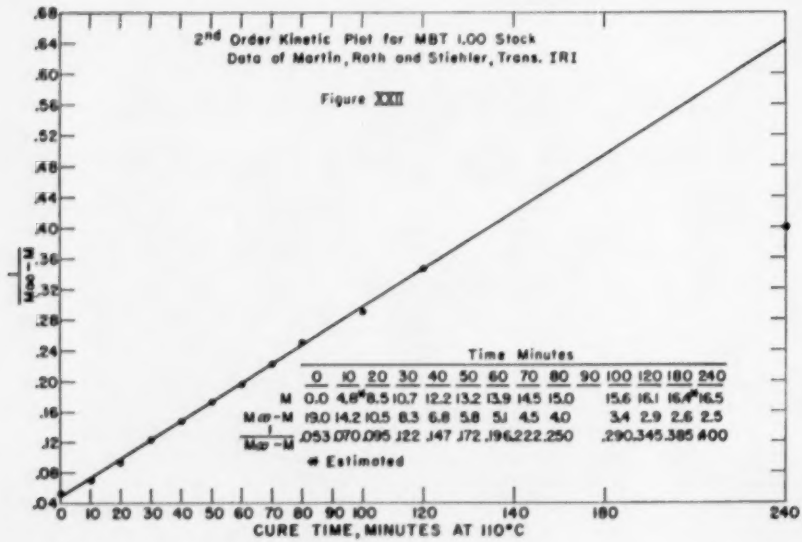
$$F = M(L^{-1} - L^{-2}) \exp A(L - L^{-1})$$

constant parameter. Parameter A changed only slightly with time of creep or time of cure and amounted to about 0.36.

Figure XXI shows the plot of M at one minute creep against time of cure at 110° C. Also shown on Figure XXI are second order kinetic plots for three values of M_∞. It is at once plain that $M_\infty = 19.0$ kg/cm^2 is nearly correct and that the reaction has an induction period of about two minutes since a shift of



the straight line two minutes to the left will cause it to pass through the $1/M$ value at zero time. Two minutes is a reasonable value for stock MBT 1.00 based on scorch measurements. Figure XXII is a table of the second order kinetic data for $M_\infty = 19.0$ kg/cm² and a plot of the data up to 240 minutes of cure.



It should be pointed out that Martin, Roth, and Stiehler found $M_\infty = 18.9$ kg/cm² as an extrapolation of the $1/M$ vs $1/t$ plot which is also a standard method for calculating effective initial concentrations of this type. Here M_∞ is considered as a measure of the effective initially usable concentration of cross-linking sites.

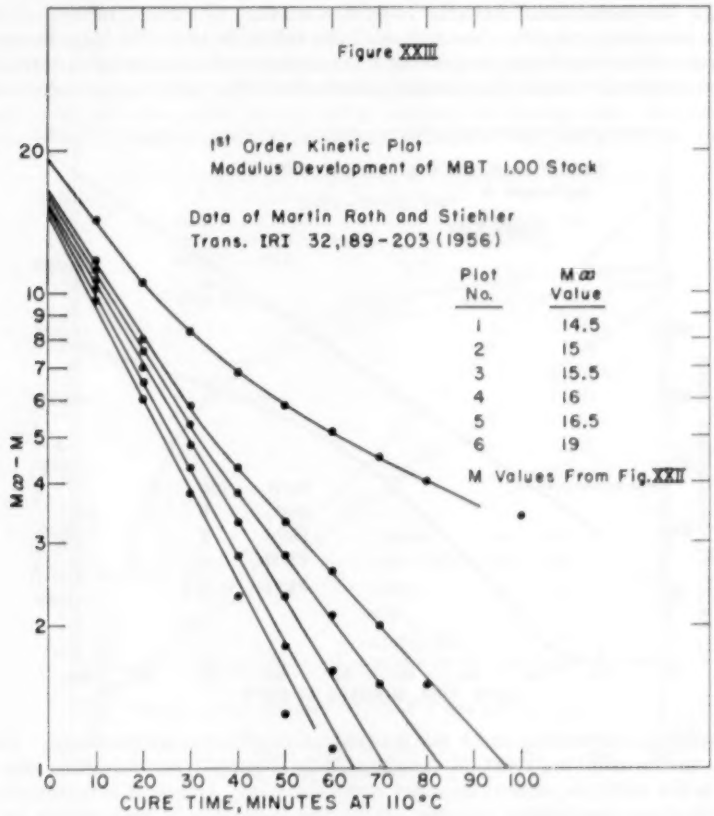
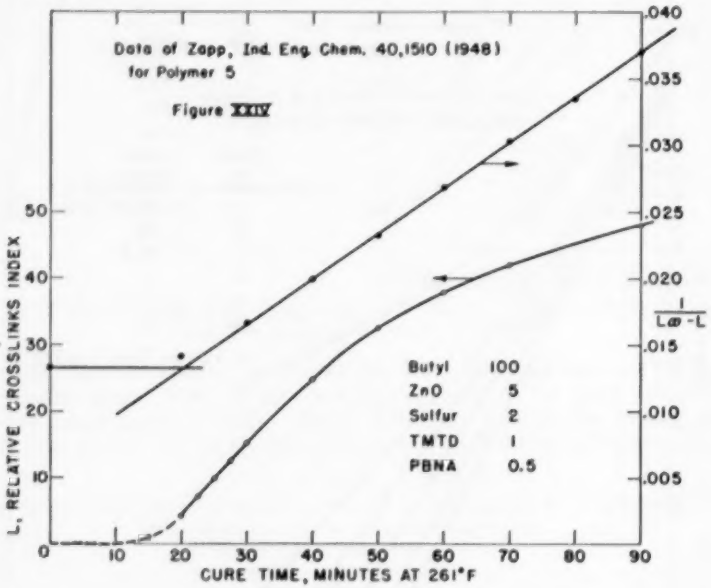


Figure XXIII consists of first order plots of the data of Martin, Roth, and Stiehler for various values of M_∞. From this we may infer that concordance with first order kinetics cannot be achieved unless an unrealistic value is chosen for M_∞, and then in certain ranges of M_∞ a two-line plot is secured.

Actually MBT 1.00 is believed to suffer reversion, even at 110° C, and if so, M_∞ should be much higher than 16.5 kg/cm², the value of M at 240 minutes of cure. This is the obvious reason for $1/(M_\infty - M)$ at 240 minutes of cure being so far below the line in Figure XXII. The kinetic approach thus illustrated considers *reversion to be any effect during vulcanization which prevents network formation or which degrades the network.*

The identification of the component whose concentration changes in accord with the second order law is perhaps the most important single item of this re-

view. Some suggestions will be attempted later, but in the first place, we can note that the concentration of isoprene units may not control directly the order of the reaction. This follows because of the ratio of isoprene units to sulfur atoms or molecules involved. Thus, in 100 g of rubber (containing 95 g of $(C_5H_8)_n$) there are 1.40 moles of isoprene units and in the recipe corresponding to this amount there are 2.50 g of sulfur, that is, 0.0098 mole of S_8 or 0.078 mole of S_1. The molar ratio of (C_5H_8) to S_8 thus is 143. The molar ratio of (C_5H_8) to S_1, assuming complete dissociation of the sulfur, is 18. The large excess of isoprene units would tend to prevent their concentration being rate controlling and would tend to make the reaction pseudo first order, that is, dependent only



on sulfur concentration or on the concentration of some intermediate. However, the crosslinking reaction experimentally is usually second order and the rate is not solely dependent on sulfur concentration. Hence, it is reasonable to assume that crosslinking depends (1) on the formation of active sites by reaction of isoprene units with the vulcanizing system, and (2) on the dimerization of these sites.

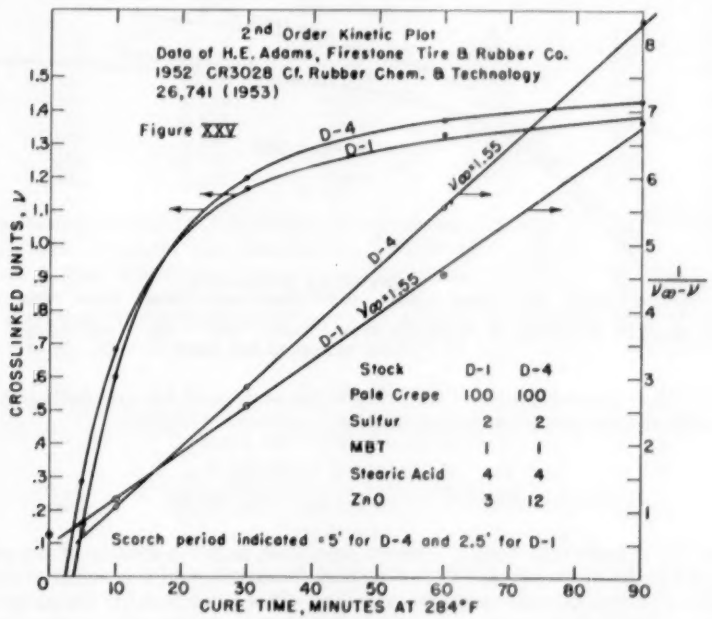
Actually Gee and Morrell[68] found the combination of sulfur for the ACS 1 recipe to follow the first order law and to be in rate about one-third that of the

ACS 1	
Rubber	100.00
Zinc oxide	6.00
Sulfur	3.50
Mercaptobenzothiazole	0.50
Stearic acid	0.50

crosslinking reaction. Therefore, the concentration of sulfur cannot directly control crosslinking. The ACS 1 recipe is sufficiently near the MBT 1.00 com-

position to make it seem safe to assume for qualitative comparisons that the sulfur in MBT 1.00 reacts according to the first order law. The data of Bergem, (e.g. Figure XI) support first order sulfur combination in MBT accelerated stocks (see the preceding section). It may further be assumed for the MBT 1.00 recipe that sulfur combination is slow in comparison to the crosslinking reaction. Several comments can be made with respect to the at first seemingly impossible situation in which the crosslinking reaction appears faster than the consumption of curing reagent.

First, some crosslinking may occur with no incorporation of sulfur in crosslinks and, second, the sulfur containing crosslinks initially formed may lose part or all of their sulfur during sulfur analysis or during cure. Information bearing on this whole problem is widely available but more data are needed.

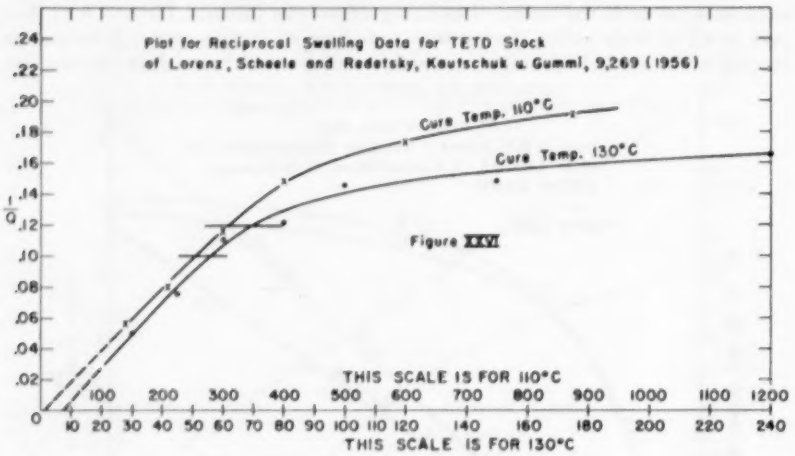


What we have includes kinetic data for formulations containing only sulfur and rubber and also some for recipes containing various concentrations of the auxiliary reagents. Various properties for following network generation in addition to modulus at low extension have been used. Here swelling data are particularly important. Portions of several studies are reviewed as follows.

Figure XXIV includes a second order kinetic plot for relative crosslinks index, L, during the cure of IIR. For these data Zapp[72] measured volume swell in cyclohexane as the index of crosslinking. Relative crosslinking was assumed proportional, in agreement with Flory and Rehner, to the 5/3 power of the polymer fraction in the swollen gel. Given in Figure XXIV also is the rate curve for development of relative crosslinks index. The sigmoid nature of the cure is evident. Zapp emphasized the sharp increase in rate at about 15 minutes. There are two points that may be stressed here. First, the kinetic

plot is a good one and, second, this is true only if the value of 75 is assumed for L_∞. L_∞ is not a measured value but is the one found by trial and error to give a straight line in the second order plot. If cure times longer than 90 minutes had been studied it is presumed that reversion would have caused L to be lower than the value calculated from $L_\infty = 75$.

H. E. Adams and B. L. Johnson[65] measured the volume swell of NR cured with sulfur, MBT and a large excess of zinc oxide. Figure XXV presents the rate curve for the development of crosslinked units, ν, and the second order



kinetic plot, assuming $\nu_\infty = 1.55$. The expression used for calculating ν, the crosslinked units per gram of polymer, is

$$\nu = \frac{1}{M_c} = \frac{V_r + \mu V_r^2 + 2.303 \log (1 - V_r)}{\rho_r V_0 (V_r^{\frac{1}{3}} - V_r/2)}$$

where M_c is molecular weight between crosslinks, ρ_r is the density of the polymer, V_0 is the molar volume of the solvent (benzene), and μ is the interaction constant of the polymer with the solvent. This is essentially the same approach as that of Zapp, ν depending on the 5/3 power of volume fraction of rubber in the swollen gel. Adams and Johnson studied the effects of variation in ZnO concentration, the data for 3 parts of ZnO instead of 12 also being given in Figure XXV. The data for the smaller concentration of zinc oxide reveal a greater tendency to revert and to scorch.

Reciprocal swelling, $1/Q$, may be taken as a measure of crosslinking. Here, Q is the weight of absorbed solvent per gram of polymer in the gel, and $1/Q$ therefore increases with state of cure. Lorenz and Echte[73] have published reciprocal swelling which gives sufficiently good second order plots. Their stock contained 2.92 of sulfur, 1.91 of MBT, and 3.72 of ZnO, all in phr. Special attention is called to the reciprocal swelling data of Lorenz, Scheele and Redetzky[74] for a tetraethylthiuram disulfide (TETD) 3.21 phr and 5.43 phr ZnO extracted pale crepe stock. The swelling data for curing at 110° and 130° are given in Table III and Figure XXVI and the data for zinc diethyldi-

TABLE III

CROSSLINKING AND SECOND ORDER KINETIC DATA FOR TETD 3.21 STOCK

Time, minute	$1/Q$	$1/Q_\infty - 1/Q$	$(1/Q_\infty - 1/Q)/0.24$	$\frac{1}{(1/Q_\infty - 1/Q)/0.24}$
		110° Cure		
0		0.24	1.00	1.00
140	0.056	0.134	0.766	1.30
210	0.080	0.160	0.667	1.50
300	0.115	0.125	0.520	1.92
400	0.148	0.095	0.395	2.53
600	0.173	0.067	0.279	3.59
875	0.191	0.049	0.204	4.90
1400	0.199	0.041	0.170	5.88
		130° Cure		
0		0.24	1.00	1.00
30	0.050	0.19	0.792	1.26
45	0.075	0.165	0.687	1.46
60	0.110	0.130	0.541	1.85
80	0.121	0.119	0.495	2.02
100	0.145	0.095	0.395	2.53
150	0.148	0.092	0.383	2.61
240	0.165	0.075	0.312	3.20

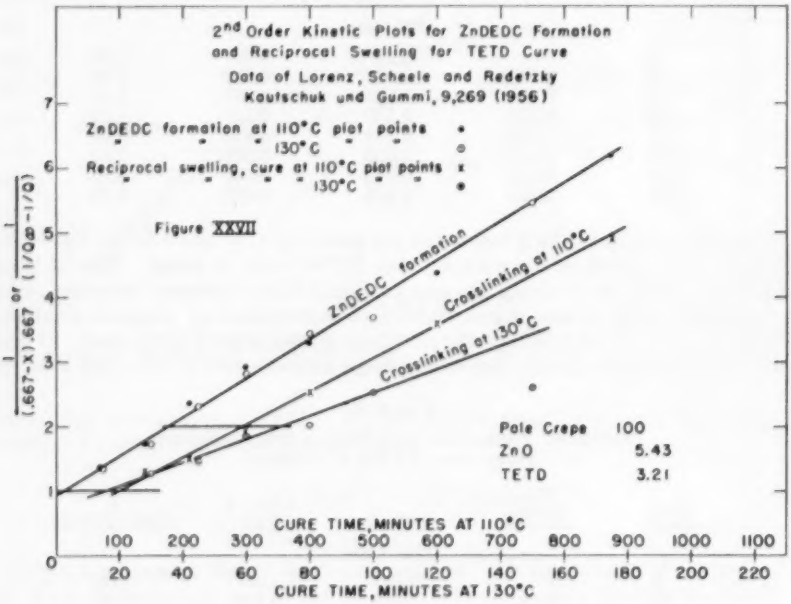
thiocarbamate (ZnDEDC) formation are given for 110° and 130° in Table IV. Scheele and coworkers have studied the TEDC cure in detail. One of their findings is that the limiting amount of zinc dithiocarbamate formation with excess zinc oxide is two-thirds (0.667) mole per mole of thiuram disulfide. Tables III and IV also include the pertinent second order kinetic data. It was desired to compare directly the second order kinetic swelling data with those of

TABLE IV

ZnDEDC FORMATION AND SECOND ORDER KINETIC DATA FOR TETD 3.21 STOCK

Time, minute	X = fraction ZnDEDC	$0.667 - X$	$\frac{0.667 - X}{0.667}$	$\frac{1}{(0.667 - X)/0.667}$
		110° Cure		
0	0	0.667	1.00	1.00
70	0.182	0.485	0.728	1.37
140	0.282	0.385	0.577	1.73
210	0.384	0.283	0.424	2.36
300	0.438	0.229	0.343	2.92
400	0.464	0.203	0.304	3.29
600	0.515	0.152	0.228	4.38
875	0.558	0.109	0.163	6.19
1400	0.610	0.57	0.085	11.8
		130° Cure		
0	0	0.667	1.00	1.00
15	0.171	0.496	0.743	1.345
30	0.283	0.384	0.576	1.735
45	0.378	0.289	0.433	2.310
60	0.430	0.237	0.355	2.815
80	0.472	0.195	0.292	3.425
100	0.486	0.181	0.271	3.69
150	0.545	0.122	0.183	5.47
240	0.602	0.065	0.07	10.3

ZnDEDC formation. Thus, in Tables III and IV the quantities analogous to concentration, c, at time, t, are $1/Q_\infty - 1/Q$ for reciprocal swelling and $0.667 - X$ for ZnDEDC formation. These, at the various cure times, are divided, respectively, by 0.24 and 0.667. Figure XXVII then is the second order plot analogous to the usual $1/c$ vs t plot. Two cure time scales are used, one for 110° and the other for 130° C. The former is five times the latter. Thus, it is at once evident that ZnDEDC formation proceeds exactly five times as fast at 130° as it does at 110° and the crosslinking rate is somewhat short of being five times as fast at 130° as at 110°. There is substantially no evidence of an induction period for ZnDEDC formation. In contrast at 110° and 130° for reciprocal swelling, the induction period, which is for these plots, the time value

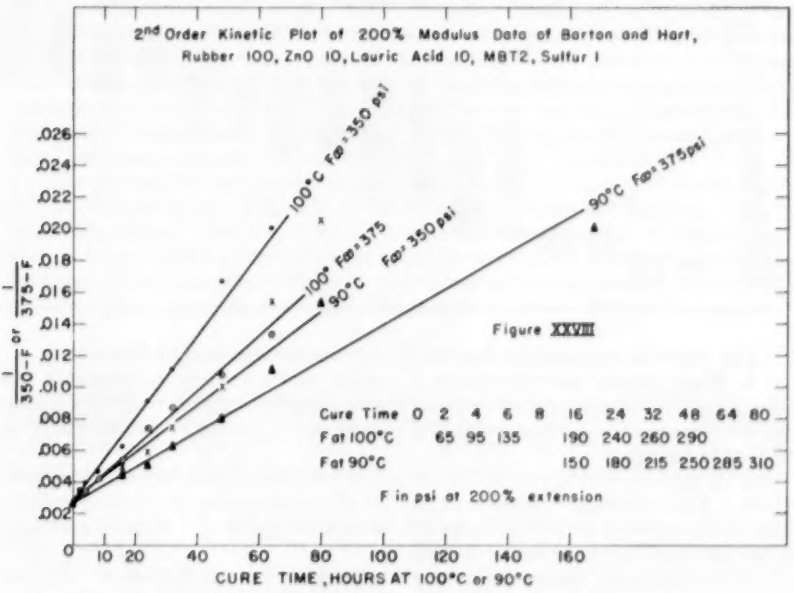

2nd Order Kinetic Plots for ZnDEDC Formation
and Reciprocal Swelling for TETD Curve
Data of Lorenz, Scheele and Redetzky
Kautschuk und Gummi, 9,269 (1956)
ZnDEDC formation at 110°C plot points
" " " 130°C
Reciprocal swelling, cure at 110°C plot points
" " " 130°C
Figure XXVII
ZnDEDC formation
Crosslinking at 110°C
Crosslinking at 130°C
Pale Crepe 100
ZnO 5.43
TETD 3.21
1/(.667-X).667 or (1/Q∞-1/Q)
CURE TIME, MINUTES AT 110°C
CURE TIME, MINUTES AT 130°C

where the line intersects the 1 ordinate, amounts to 100 minutes and 16 minutes, respectively, although the scatter of the data is such as to permit drawing of the line for 110° C through the 1 ordinate at 20 minutes. This would give an induction period just one-fifth that at 110°.

Figure XXVI shows the reciprocal-swelling rate curves for the data of Table III. This figure, understandably, gives no indication of an induction period or of reversion and does less well than Figure XXVII in comparing crosslinking rates. It should be pointed out that the induction periods estimated from Figure XXVII are real to the extent that the second order approach to crosslinking has a basis in fact. Of course it is known that TETD possesses delayed action.

Barton and Hart[64] studied the effects of temperature and time of cure, as well as the effects of the concentrations of sulfur, MBT, ZnO, and lauric acid, on vulcanization as revealed by modulus at 200 per cent extension. Their

work typifies the compounders approach in which a large number of experiments must be run in order to ascertain the response to a large number of variables, the response being directed toward a certain arbitrary end. It is clear from Barton and Hart's work that the modulus at 200 per cent extension is directly proportional to combined sulfur as well as to sulfide sulfur provided that time, temperature and concentrations of zinc oxide, fatty acid and accelerator are chosen to give the maximum yield of crosslinks. In this work sulfur concentrations of 0.40, 0.65 and 1.00 phr were used, the recipes being purposely "starved" in crosslinking agent. The higher the sulfur concentration the higher is the concentration of auxiliary agent that must be used for attainment of maximum modulus is a conclusion that may be drawn from this work. A further important result was that the maximum modulus was higher



at 90° C than at lower or higher temperatures of cure. Figure XXVIII and Table V reproduce data of Barton and Hart with respect to temperature. They were not especially interested in kinetics but merely used a "sufficient" time.

There is a kinetic explanation for the temperature of maximum modulus as observed by Barton and Hart. At temperatures below 90° the active sites are formed so slowly that they can in part disappear by scission (a first order process) or by other side reaction rather than disappear by taking part in the second order crosslinking reaction. The kinetic plots for 90° are poor but those for 100° are good. The data in Table V show that even at very long times of cure at the low temperatures a low modulus develops. For the intermediate temperatures, however, if the cure times are not too short, a high modulus is found. Reversion in this stock should be apparent at times longer than those reported on, however. Even at the higher temperatures, according to the commonly

accepted understanding there is no evidence of reversion in these data. The kinetic approach to the study of the data, however (cf. p. 1323) reveals the existence of a scission effect. This effect, here, is probably associated with scission having a higher temperature coefficient of rate than the crosslinking rate. At the low temperatures, though scission is slow, it still is possible because of its first order nature whereas the second order crosslinking process below a certain concentration level of active sites cannot occur.

TABLE V

MODULUS* AND SULFIDE SULFUR* AT VARIOUS TIMES AND TEMPERATURES OF CURE

Time of cure, hours	70° C		80° C		90° C		100° C		110° C		120° C		140° C		160° C	
	F	S	F	S	F	S	F	S	F	S	F	S	F	S	F	S
0.25															155	0.29
0.50													165	0.25	180	0.36
0.75													195	0.31	180	0.38
1													200	0.37	180	0.43
2							65	0.04	110	0.10	165	0.17	210	0.42		
4							95	0.08	160	0.21	200	0.26				
8							135	0.14	210	0.26	250	0.36				
16					150	0.14	190	0.22	265	0.37	260	0.42				
24					180	0.18	240	0.30	280	0.41						
32					215	0.21	260	0.32								
48					250	0.26	290	0.37								
64					285	0.31	300	0.40								
80					310	0.32	300	0.42								
168					325	0.37										
252			265	0.34	320	0.39										
336			265	0.36												
432	210	0.27														
528	210	0.28														

* Modulus = F at 200% extension, in psi, and sulfide sulfur = S, in phr.

The material reviewed in Section V may be summarized as follows:

1. When ample concentrations of sulfur and auxiliary components are present and a suitable temperature is chosen, crosslinking as revealed by modulus development or volume swell is a second order process, experimentally as well as in theory.

2. A possibly useful concept of reversion has arisen from kinetic considerations. This considers reversion as any effect which lowers the rate of generation of the network as well as those effects which degrade it. Kinetic reversion is no less real than common reversion.

3. An optimum temperature can be expected in vulcanization. At low temperature, reactive crosslinking sites may be too few to crosslink, thus permitting no reaction or a certain amount of cleavage, while at high temperature reversion may occur after the crosslinking step.

4. The crosslinking (vulcanization) of an elastomer depends on (a) the formation of active sites in sufficient number by reaction of chain segments with the curing system so that (b) they can dimerize to form crosslinks rather than cleave or disappear by some other reaction.

VI. THE CHEMISTRY OF VULCANIZATION WITH SULFUR. THE COPOLYMERIZATION THEORY

Almost no one questions that α-methylenic hydrogen atoms and double bonds in NR react with sulfur during cure to form intermolecular links. It is commonly believed too that most of these links contain sulfur. In contrast, peroxide curing leads to C to C crosslinks by way of a substitutive process.

This, according to recent fundamental studies of Moore and Watson[76b], may even be quantitative provided 10 phr of *tert*-butyl peroxide are used. The term quantitative, here, means that the number of crosslinks introduced can be related stoichiometrically to the number of molecules of peroxide reacted. Cyclization, an expected reaction in this type of cure, would use up double bonds, but, understandably, would not interfere with the quantitative yield of crosslinks. Moore and Watson suggest crosslinking with decamethylene dismethylazodicarboxylate, which previously had been thought quantitative, to be relatively inefficient as compared to peroxide linking. It is worth noting further that neither peroxides nor dis-azodicarboxylates cure butyl but instead exert a scission action on this relatively stable elastomer. On the other hand, it is sometimes implied that the systems sulfur-accelerator-ZnO-fatty acid and TMTD-ZnO, which cure this polymer nicely, are not quantitative. Although existing knowledge of sulfur or TMTD chemistry related to curing is often said to be meager, the action of these agents, nevertheless, is so effective and so important commercially that review of their curing action should not be passed over lightly. Perhaps the need for more fundamental knowledge about these reagents is so great that what we have merely seems meager. Existing practical information about sulfur vulcanization is widespread, usually is exact only for some particular purpose, and often is of limited value scientifically.

The purpose of the present section is to review some of the chemistry of sulfur vulcanization. This will be done in part under the heading "copolymerization theory" but an effort will be made to arrange most of the information under suitable subheads so that it can be used easily by the reader for any purpose. TMTD curing will be considered as a limiting case of linking polyisoprene chain segments through sulfur atoms.

VIA. THE EFFECTS OF ZINC OXIDE

Zinc oxide[93] is not an accelerator but its presence in a rubber-sulfur mix leads to higher modulus values during cure, i.e., to tighter cures. Considerations presented in this section lead to the view that zinc oxide affects the mechanism of reaction but first some comments should be made about another proposal.

According to the salt crosslink theory[66] of vulcanization, zinc oxide reacts with polar groups attached to rubber molecules, the polar groups being present initially or introduced by the vulcanization system. Two sets of data, one for butyl and the other for natural rubber, indicate that this cannot be an important function for this type of activator.

Zapp and coworkers[59] were able to remove zinc oxide from swollen butyl (IIR) vulcanizates by reaction with oleic acid and extraction of the zinc oleate produced with benzene. Obviously the polymer in their mixes was not converted to a soluble form and any remaining zinc must have been present as zinc sulfide. Such evidence against the frequent occurrence of zinc salt crosslinks appears to be adequate but, in addition, Zapp and coworkers were able to deduce that the crosslinks probably contain two sulfur atoms each and that, when reversion sets in, thiol groups are formed. They were able to solubilize some IIR vulcanizates by treatment with hydrogen sulfide and subsequently to "revulcanize" them with oxidizing agents.

Hydrogen sulfide is liberated by hydrochloric acid in the presence of a swelling agent from IIR cured with sulfur-zinc oxide-accelerator, but the treatment of cured IIR stocks with oleic acid does not remove zinc sulfide. This salt in

butyl mixes is thus shown to be stable toward weak acids and it is, therefore, of interest to note that ZnS is a good activator for TMTD curing[77]. Also in nonrubber systems it is oxidized by TMTD to form sulfur and ZnDMDC. In cured rubber it was found that dimethylammonium dimethyldithiocarbamate (DMADC), actually produced *in situ* from CS_2 and $(CH_3)_2NH$, did not react with ZnS[78]. This nonreactivity toward certain ionic reagents thus appears to be related to the insolubility of ZnS which property does not, however, prevent the presumably radical type oxidizing action of TMTD on sulfide sulfur to form free sulfur in the absence of rubber, or, in the presence of rubber, crosslinks without free sulfur.

The shortpath distillation of TMTD cured or sulfur-cured NR stocks after treatment with DMADC, though not affecting zinc sulfide, does remove most of the zinc as volatile ZnDMDC. This constitutes a fairly general technique[78] for removing zinc from rubber. It was found that carboxyl groups attached to rubber in the case of TMTD cures were probably converted to dimethylamide[79] groups so that the zinc salt of NR, otherwise expected, was not formed during the DMADC-shortpath distillation procedure.

Zinc oxide or other metallic oxide is not absolutely necessary for getting a fairly satisfactory state of cure. Thus, sulfur curing with aldehyde-ammonia or butyraldehyde aniline[36] leads to snappy, rather transparent vulcanizates. Barton[37] found that numerous oxidizing agents, including MBTS, could be used in place of zinc oxide but, in general, the vulcanizates were of poor quality. For the most important cures, zinc activation is necessary. The point to be made here is that curing does not require zinc atoms. A second point, in passing, is that zinc oxide and certain oxidizing agents may have a common action during curing as reported by Barton, but zinc oxide is not, therefore, necessarily an oxidizing agent. In accelerated sulfur curing and probably in sulfur curing, sulfur is an oxidizing agent. This will be considered later. Occasionally some workers consider ZnO to be an oxidizing agent in vulcanization.

When zinc oxide is a component in a vulcanizing sulfur-accelerator-fatty acid mix, zinc sulfide might be an expected product because the α-methylenic hydrogens should react with the sulfur to form H_2S which is known to attack ZnO. Bergem's data, discussed in Section IV, showed a constant proportion of combined sulfur to exist as zinc sulfide during the course of vulcanization. Adams and Johnson[65], however, reported that zinc sulfide formation is to be identified with reversion. This is opposed to the Armstrong, Little and Doak[80] proposal that curing occurs by way of zinc mercaptide derivatives of polyisoprene which, they believed formed one equivalent of zinc sulfide per mono sulfur or di sulfur crosslink. Considerable support for and against this view was contributed by Hull, Olsen and France[81], as well as by Barton[64] who recently found about one sulfur atom per crosslink for *optimum cured* MBT mixes. As Bergem and many others have pointed out and as is still true for most well-cured stocks, ZnS content is not a measure of state of cure (crosslink density). All of the above groups[64,65,79,80,81] of workers were concerned with soluble zinc compounds, including zinc sulfide, *not as ZnS* but as various mixed salts made up of sulfide ions, zinc ions and miscellaneous anions, including rubber carboxylate ions. They did not seem to recognize any important buffering effect on hydrogen sulfide activity inherent in such systems.

C. R. Park[99] confirmed Dinsmore's finding[91] that one volume phr of zinc oxide increases the modulus of rubber-sulfur cures more than an equal volume of channel black but he considered this not to be a reinforcement effect. Others have said such a low loading of zinc oxide causes scorchiness. Magnesium

oxide is also a stiffener in low concentration as are many diamines. Williams[20] found that the modulus of sulfur vulcanizates could be increased by "swelling in" zinc propionate. Clearly the more recently demonstrated behavior of rubber as an acid must be considered here. The NR molecule appears to have carboxyl groups[75] at many of the chain ends. To the extent that this is the case, the salt-forming-stiffening effects of polyvalent metal derivatives and polyamines is a case of main polymer chain extension. Some salt crosslinking probably occurs as a result of an occasional internally situated acid group.

It is reasonable, if thiol groups were formed during cure, to expect that zinc oxide would convert them to zinc mercaptide linkages. But these linkages would be like soluble salts of weak acids and would be unstable in the presence of the stronger fatty acids and salts which exist in most vulcanizates. Zinc dodecyl mercaptide (2 phr) in extracted rubber was found to be a weak activator of MBT-ZnO acceleration. When palmitic acid (2 phr) was also present an inhibiting action was observed, due presumably, to the liberation of free mercaptan. The free mercaptan, though a weak acid, is, nevertheless, known to be an inhibitor when added as such and possesses a high reactivity toward radicals.

Zinc oxide shows very little tendency to react with sulfur and surprisingly little tendency to react with TMTD. The more or less forced reaction of TMTD[104] and excess ZnO forms sulfur as well as most of the zinc salts and gases that would be expected from oxygen-sulfur interchange superimposed over a general decomposition of TMTD involving all bonds except those of the methyl group. The products isolated or detected from this reaction included CO_2, COS, CS_2, S_8, ZnDMDC, $(CH_3)_2NC{:}SN(CH_3)_2$, TMTM, and $(CH_3)_2NH$. The same products except for sulfur were isolated or detected in rubber cured with excess ZnO and TMTD and in addition a small amount of hydrogen was detected. The mass spectrometer[94] was used for detecting the gases. Oxygen-sulfur interchange is a promising field for future study.

The complex nature of zinc salts in vulcanizates leads naturally to the effects of hydrogen sulfide which is the subject of the next section.

VIB. THE EFFECTS OF HYDROGEN SULFIDE

Early in the study of accelerated sulfur vulcanization Bedford and Gray[82] were concerned with hydrogen sulfide as a precursor to ZnS. Their method for the determination of ZnS, essentially that of Stevens[83], involved treatment of the sample with hydrochloric acid in ether solutions. This method converts zinc sulfide sulfur quantitatively to hydrogen sulfide whereas only the socalled "soluble" zinc sulfide reacts with oleic acid or with DMADC as described in Section VIA.

Bedford and Gray made a number of important findings with respect to H_2S. For example, they found its complete removal to be unfavorable to TMTD vulcanization, whereas they reported a small amount to enhance it. Booth and Beaver[84] reported a large excess of H_2S to be inhibitory for all types of sulfur curing. Craig, Davidson and Juve[79,85] suggested a possible relation between the number of sulfur atoms per crosslink and the buffering capacity of zinc-containing systems and this possibility has been confirmed by Farmer, Ford and Lyons[95] with low molecular weight olefins. They found fewer sulfur atoms per crosslink when zinc oxide was present. The former workers along with Semon and Hay[86] reviewed the previous studies having to do with the effects of zinc oxide and hydrogen sulfide.

Recently unsuccessful efforts have been made[87] to detect H_2S over vulcan-

izing mixes compounded in the ACS 1 recipe as well as in TMTD-ZnO recipes. In this work the uncured stocks were placed in break-seal tubes which then were evacuated, sealed off and heated for various periods at 130° C. The tubes were finally attached to the mass spectrometer sampling system and the spectra of the evolved gases determined. No H_2S was found and none was expected because of the known absorbing efficiency of ZnO in admixture with the other auxiliary substances. The formation of free H_2S during the later stages of hard rubber cure has been known of for a long time but H_2S is not evolved during the crosslinking period in accelerated soft rubber vulcanization under the usual conditions.

The problem of the concentration of H_2S during vulcanization is really the problem of soluble sulfide concentration. This is known to be low and can be presumed dependent on any metallic ions which are present. Some of the effects may be studied[88] effectively by compounding oxides and sulfides and noting the activating properties that develop. Thus cadmium sulfide as well as ZnS activates TMTD cure. Both CdS and ZnS are nearly insoluble in rubber. Zinc oxide is even more active than the sulfides but CdO is inactive and usually is inhibitory. It is known that TMTD does not require fatty acid, i.e., TMTD cure presumably needs an acidity level that is low, perhaps near neutrality. MBT, itself an acid, and those other accelerators for sulfur cure which form MBT *in situ* do require a higher acidity level and fatty acids are commonly used. For such accelerators, cadmium oxide is more active than zinc oxide. More striking still, in support of this overall view, is that CdS is quite active and ZnS inactive for the activation of MBT acceleration. CdS evidently liberates sufficient H_2S for curing but ZnS liberates too much. The ability of ZnS and CdS to react with MBT, to produce different effects in contact with sulfur and rubber probably involves the attack of benzothiazolyl radicals. The strength of MBT as an acid does not alone seem adequate to account for these effects.

The reason for the pronounced retarding action shown by low (impurity) concentrations of cadmium oxide in zinc oxide for use in TMTD activation is thus at hand. The cadmium ion simply reduces the sulfide concentration to a level too low for good curing. Compounders have been aware for a long time that the presence of cadmium in zinc oxide is not harmful for activation of MBT recipes.

The most obvious way of regulating H_2S concentration in rubber is by way of acid-base buffering. Amines, oxides, acids, and solid pigments often are present in rubber mixes which combine to give buffer systems of varying buffering capacities.

The H_2S regulating effects contributed by carbon black have been considered by Studebaker and Nabors[106]. The regulation, which seems appreciable, appears to depend on the redox and catalytic features of the carbon black-rubber systems in which air, sulfur and other auxiliary substances are important.

VIC. THE EFFECTS OF ACIDS, BASES AND WATER

Fatty acids, both saturated and unsaturated, occur in NR and are common additives. They are known to contribute various effects. The more commonly recognized ones may be listed as follows, some of them not being essential to vulcanization:

1. Fatty acids are a source of hydrogen and carboxylate ions for buffering the curing system, especially in the presence of zinc oxide.

2. They have a solubilizing effect on zinc and other metal ions and on organic bases.

3. They are a source of H atoms for radical reactions, especially the unsaturated acids which also show double bond activity, toward curing and aging (see Section VII).

4. They affect the rate of crystallization[102]. Bergem[93] reported that they raise the T-50 value of cured gum mixes.

5. They soften NR physically and also they degrade NR chemically at curing temperatures because of their acid properties.

6. They help in certain mixing operations, e.g., in reducing sticking to the surfaces of mixing equipment. They aid in dispersing ZnO and some technologists believe they can act as dispersants for carbon black.

The rate of sulfur combination with NR is not much affected by the presence of fatty acid, even in the presence of ZnO and MBT. This was discussed in Section IV where it was pointed out that a constant fraction of combined sulfur tends to be converted to ZnS sulfur during the course of vulcanization. Fatty acid increases the size of this fraction.

The really important effect of stearic acid is to enhance the effect of ZnO in promoting modulus development (crosslinking) with respect to both rate and final state attained. This behavior is probably limited to the cure period. Thus for a well-balanced MBT stock, MBT displaying a very short scorch period, the modulus is increased by increased amounts of stearic acid. The rate of curing during the scorch period is decreased by increased amounts of acid and the tendency toward reversion may also by increased. The length of the scorch period is increased by fatty acid.

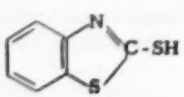
TMTD vulcanization is notable for not requiring the presence of fatty acids. This is clearly related to the formation during cure of dimethyldithiocarbamic acid which promptly reacts with zinc oxide to form ZnDMDC so that the system is more or less self buffering. Fatty acid is required for the TMTM or TMTD acceleration of sulfur cures because during the curing period with these reagents the acceleration following the induction period is really ZnDMDC acceleration which requires fatty acid. This type of cure is very rapid in comparison to TMTD cure and with it reversion is much greater than for TMTD curing. With TMTD curing, ZnDMDC is merely a stable end-product.

Acids, in general, seem to retard, i.e., extend the scorch period and stearic acid is no exception. Stronger acids such as phthalic, benzoic and salicylic acids, which were discussed in Section III, are more potent than fatty acids. Salts, e.g., zinc chloride, which hydrolyze to strongly acid solutions, are strongly inhibitory. The results depend on the concentration as well as on the acid strength of any particular acid. Thus, though benzoic acid is an effective retarder for well-balanced stocks, in acid-poor stocks small amounts effectively activate acid-type accelerators such as MBT and other thiazole thiols.

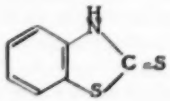
The thiazole thiols constitute a special type of acid in the field of vulcanization. In fact, due to the importance of MBT and some of its derivatives as accelerators, vulcanization cannot be effectively reviewed without extended consideration of the thiazole thiols. Here the behavior of MBT as an acid will be mentioned; its action as an accelerator will be taken up later.

Chemical Abstracts "defers to usage" in the case of MBT and uses the name 2-mercaptobenzothiazole rather than benzothiazole-2-thiol. This seems a pity to some investigators who are aware that various instrumental techniques, which here seem definitive, show MBT not to be a thiol. The trouble is that

neither do they clearly show MBT to be benzothiazoline-2-thione. The prob-



Mercaptobenzothiazole



Benzothiazoline-2-thione

Hypothetical Tautomers of MBT

lem as to structure can be resolved if the view of Hunter[111] is accepted and MBT is considered to display mesohydric tautomerism. Neither tautomeric form is capable of existence. The single form which has been isolated is a polymer of monomeric units joined through H bonds. This view accounts for the behavior of MBT as an acid. Since neither thiol nor thione forms can exist in the monomeric state and since they are about equivalent for writing reactions we probably should retain the established name mercaptobenzothiazole.

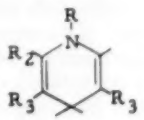
Bases in sharp contrast to acids are accelerators. Lead, calcium and magnesium oxides, which were Goodyear's accelerators, are still used to a limited extent, mainly at high temperatures. Zinc oxide in contrast is not an accelerator. An inorganic base (inorganic bases require fatty acid) in order to be an accelerator probably must be able to react with sulfur. Zinc oxide does not do this, at least up to 140° C.

Two papers, one by Newton[96], the other by Newton and Willson[97], concerning the effect of nonrubber components on vulcanization rate, contributed significantly to the problem of buffering. Newton found an increase in water concentration to slow down the rate of cure of mixes containing buffer systems of pH lower than about 6.6 (the pH was measured in 1/15 *M* buffer solution). If buffer systems of pH higher than 6.6 were included in the rubber-sulfur mixes then the addition of water increased the cure rate. Newton and Willson found that the nonrubber components contributed a rather massive buffering effect as measured by the effect of various concentrations of phosphoric acid on cure rate. Cure rate at 298° F was measured by the time required to develop 2100 psi modulus at 800% extension. Newton and Willson considered the effect of zinc oxide in the ACS 1 recipe to consist of something more than "assisting the acid-base equilibrium toward alkalinity". They stated further, "There are also other factors in these tests which act to lower concentration of hydrogen sulfide; namely, the quantity of sulfur is lower in the MBT mix and the temperature of cure is lower". Among the important features noted in Newton and Willson's work was the solvent-type effect of water. It enhanced during cure the retarding effect of acidity and the activating effect of basicity. Bloomfield[109] later reported that 0.75 phr of MBT in NR requires water for maximum accelerating effect in the recipe containing sulfur 3 phr, ZnO 5 phr, stearic acid 1 phr, and MPC black 30 phr.

Special classes of organic bases such as DPG, the socalled aldehydeamines, and the thioamines call for some comment in this section. The diaryl guanidines are strong organic bases which as accelerators require zinc oxide and fatty acid for best rates and properties. The stocks are scorchy, tend to revert and are poor aging. It seems best to leave a review of their behavior to a later reviewer.

The aldehydeamines of greatest interest in a review of vulcanization are those made under very weakly acidic conditions from primary amines and straight chain aliphatic aldehydes having three or more carbon atoms. These

products are not single individuals but the main components[36] in each case appear to be more active as accelerators than the minor components. The general formula for the "active" agent is:



These dihydro pyridines are strong reducing agents. They react rapidly with sulfur[36]. In the presence of acids and various oxidizing agents, including sulfur, they form substituted pyridinium ions. No doubt these ions are important endgroups for terminating sulfur chains in precursor reactions to crosslinking. It has not been possible to prepare a dihydro pyridine in the case of acetaldehyde[98] and any primary amine. Presumably the expected product, when R_3 is H, is too unstable and a different type of reaction product results. The accelerator called acetaldehyde-aniline is not a simple dihydro pyridine. Propionaldehyde[98] gives a fair yield with aniline, butyraldehyde[36] higher, and heptaldehyde[98] still higher. Heptaldehyde-aniline was referred to by Cadwell[99] as one of the most powerful known accelerators for gum stocks. It is sold under the name "Hepteen Base".

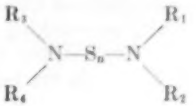
Aldehydeamines of the dihydro pyridine type are sometimes referred to as good aging accelerators. They are poor in this respect as compared to MBT and they tend to revert. They do not require activation but do work better if zinc oxide and fatty acid are present.

Organic bases of simple structure were important among the early organic accelerators. The basic strength, however, of such compounds is only a secondary property with respect to their effects on cure rate or state of cure. Of some significance to the overall vulcanization problem is the fact recently reported by Scheele that tertiary amines are not accelerators, secondary amines are feeble, but that primary amines, depending on their basic strength, are quite active. The tests reported were mostly on aromatic amines.

A recent study[88] has been made of the effects of the three classes of simple aliphatic amines on thiazole type accelerators. The thiazoles MBT and MBTS were chosen as the accelerators. Decylamine, di-*n*-amylamine, and tri-*n*-amylamine were chosen as representative of the three classes of amines. The recipe used consisted of ZnO 5, stearic acid 1, sulfur 2.5, PBNA 1, and MBT or MBTS 1. The amines were tested in 0.1 and 0.5 concentrations, all quantities being in phr of NR. The tertiary amine had no activating effect, the secondary and primary amines were potent activators, especially the primary. This study was suggested by a previous finding of Craig, Robinson and Fowler[105] that primary and secondary but not tertiary amines shortened the induction period for the reaction of TMTD with acetone.

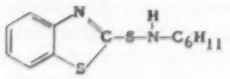
The results of the various acids, bases and accelerators suggest that replaceable hydrogen in the vulcanizing system is important in the overall process. Acid anhydrides, for example, phthalic anhydride, have a special retarding effect in that they can convert primary and secondary amines to phthalamides.

The thioamines of interest in vulcanization have the structure:



They are vulcanizing agents. One in commercial use is 4,4′-dithiobismorpholine (Sulfasan R) or morpholine disulfide. This reagent displays delayed action which may be controlled and manipulated to a certain extent by use with delayed action accelerators, e.g., MBTS. It consists of sulfur chains two atoms long terminated in amino groups. With respect to the shortness of the chains it is like TMTD or sulfur monochloride. It has been claimed that the thioamines to some extent do away with the need for zinc oxide. In one case it was reported that dimethylamino monosulfide[86] was a mild crosslinking agent in the absence but not in the presence of zinc oxide.

Related in structure to the thioamines are the thiazole sulfenamides of which N-cyclohexyl benzothiazolylsulfenamide is an example. It has the structure:



and is sold under the tradename Santocure. Accelerators of this type display a long scorch period.

VII. THE REACTIONS OF ISOPRENE UNITS

Cumyl peroxide and *tert*-butyl peroxide crosslink natural rubber quantitatively under certain conditions by way of C to C crosslinks. The process is substitutive (see the introduction to Section VI).

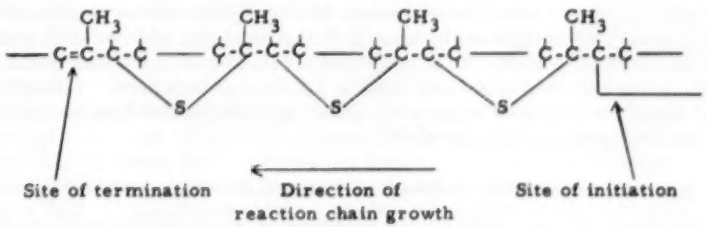
Farmer, Ford and Lyons[95] studied various sulfuration procedures with low molecular weight polyisoprenes. They found crosslinking at 0° C with H_2S and SO_2 (the Peachey process) to be wholly disubstitutive, to lead to S_4 crosslinks, and suggested that the mechanism involved S_2 radicals. At higher temperature (83°) substitutive-additive crosslinking occurred to some extent. For the model olefin, 2,4-dimethyl-2-pentene with sulfur-ZnO-zinc dibutyldithiocarbamate and H_2S activation at low temperature, substitutive S_4 crosslinkage was predominant and even at 140° C the crosslinks tended to contain four sulfur atoms and the process remained substitutive. Also, with TMTD and this olefin in the presence of zinc oxide at 140°, the process was disubstitutive but the crosslinks contain only one or two sulfur atoms. In the absence of ZnO the process was partly additive. There was no evidence of C to C crosslinking. α-Toluenethiol and butanethiol with H_2S and SO_2 gave the corresponding tetrasulfides. Some of the byproducts of the various sulfurations were not isolated and may constitute additional modes of crosslinking, according to the authors.

The reactions of the isoprene units in NR usually are far from quantitative, especially in the case of radical type reagents. However, some ionic type reagents react virtually quantitatively. Thus the addition of HCl to form rubber hydrochloride and the cyclizing action of strong acids belong in this classification. Cyclizing requires isoprene units two at a time. According to Gordon[112] this leaves about 13.5 per cent uncyclized units. These as well as the cyclized units may engage in crosslinking and it is known that rubber cyclized in bulk is ordinarily insoluble and requires mill breakdown for the preparation of smooth adhesive cements. The crosslinking caused by the action of strong acids involves proton transfer, a form, in the case of rubber, of α-methylenic activity. The crosslinks are C to C. In the behavior of the isoprene units, to

a first approximation, it appears that hydrogen atom transferability goes hand in hand with proton transferability.

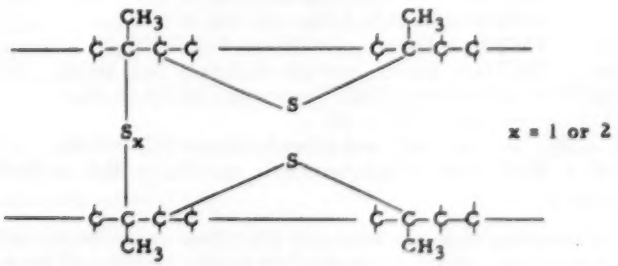
Neither strong acid crosslinking nor peroxide curing ever is sufficiently intense to form hard rubber. Sulfur and rubber in contrast, readily form hard rubber and when conditions are relatively mild the product when reaction ceases contains 32 per cent sulfur and 68 per cent polyisoprene corresponding to one sulfur atom per isoprene unit. Double bonds are still present according to infrared studies but probably a majority of those originally present have reacted. Prior to the infrared studies it was commonly believed that hard rubber was nearly free of double bonds and that sulfur atoms had added one at a time either intra- or intermolecularly to form the fairly rigid three dimensional network. Midgley, Henne, and Sheppard's study[107] of ebonite pyrolysis products established the presence of at least some tetrahydrothiophene units. The following structure (Formula I) and mechanism based on their data is obviously oversimplified:

Formula I



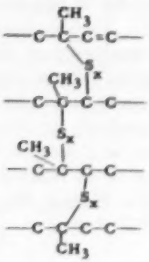
Such a structure would be favored by conducting the hard rubber reaction in dilute solution in a good solvent but no work seems to have been reported on this, though in 5 per cent dichlorobenzene solution, according to Whitby and Jane[56], a tenfold excess of sulfur at 140° C forms a product containing precisely 32 per cent sulfur and 68 per cent isoprene units. The recent report of Glazebrook and Saville[108] that diethylamine-sulfur-1,5-diolefin reaction products probably contain tetrahydrothiophene residues makes Formula I worth serious study. They suggest Formula II and present a polar mechanism to account for its formation, though they do not completely exclude radical mechanisms or the coexistence of radical and ionic routes.

Formula II



The fact that Glazebrook and Saville were able to support Formula II by finding evidence for structures made up of three olefin units linked through sulfur, makes it desirable to consider an openchain analog of II, shown as Formula III.

Formula III



The important features of Formula III are (1) that it illustrates the linking of several 1,5-diene units through several blocks of sulfur atoms, thus constituting a crosslink copolymer chain, and (2) that it is wholly additive with double-bond and hydrogen shift. It is noteworthy that the data of Glazebrook and Saville do not *exclude* doublebond shifts in 1,5-diene sulfurations. Linnig[109] has found further evidence to support Sheppard and Sutherland that doublebonds do shift during the sulfuration of NR.

VIE. THE COPOLYMERIZATION THEORY OF VULCANIZATION

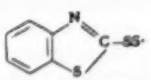
This theory[86], now needing some modification, proposes that isoprene units in NR can copolymerize with blocks of sulfur atoms to give crosslink copolymer chains (see, for example, Formulas II to VI). The mechanism is by way of a redox system in which, sulfur or a polysulfide, is the oxidant and H_2S, or an H_2S precursor, the reductant. In agreement with the theory, H_2S in very low concentration initiates sulfur curing but in excess it retards or inhibits. The properties of zinc oxide and fatty acid as activators are particularly well-accounted for by the theory. These had previously seemed mysterious. The following types of reactions are believed to occur to varying extents during the three stages of vulcanization and are intended to suggest the *buffering action* on H_2S concentration to be expected of simple curing systems.

1. Polyisoprene + (S) $\longrightarrow$ H_2S + polyisoprene radicals
2. $ZnO + H_2S \rightleftharpoons Zn(OH)SH \longrightarrow ZnS + H_2O$
3. $ZnO + RCOOH \rightleftharpoons Zn(OH)OC(O)R$
4. ZnO + MBT $\rightleftharpoons$ H_2O + the zinc salt of MBT
5. ZnO + TMTM + H_2S $\longrightarrow$ H_2O + ZnDMDC
6. ZnO + TMTD + H_2S $\longrightarrow$ (S) + H_2O + ZnDMDC
7. TMTD + (S) $\rightleftharpoons$ (TMTT) $\rightleftharpoons$ TMTM + (S_2)
8. TMTD $\rightleftharpoons$ TMTM + (S)
9. $S_8 + H_2S \rightleftharpoons HS_8H$ and other hydrogen polysulfides
10. ZnO + MBT + S_8 + H_2S $\longrightarrow$ S_1 or (S_2) + H_2O + Zn(SH) salt of MBT

Some of these reactions are ionic and the others are probably radical-type oxidation-reductions. Individually they are simple enough and are useful but

taken together they may make the vulcanization process seem more complicated than it really is.

The copolymerization theory attempts to account for the scorch period in vulcanization on the basis of (1) cleavage of polyisoprene radicals while they are too few in number to crosslink and (2) the formation of enough H_2S to initiate the copolymerization. Delayed action accelerators and vulcanizing agents are efficient chemical softeners and in contact with ZnO they are efficient absorbers of H_2S. For example, MBTS in contact with ZnO and H_2S will tend to liberate S and the zinc salt of MBT. The sulfur will not be free but probably will be present as a benzothiazolylthiyl radical:



This should be more stable than a free S_1 or S_2 diradical but should be reactive enough to supply sulfur atoms as needed for abstracting hydrogen to give additional polyisoprene radicals for cleavage or later for copoylmerization. As soon as the delayed action accelerator is consumed, the system becomes a zinc oxide-sulfur-MBT system and sufficient H_2S will be available to liberate benzothiazolyl mono or polysulfur radicals for copolymer chain growth, termination and initiation.

The suggestion that delayed action is to be related to polyisoprene chain cleavage is a modification of the original theory. Cleavage may result from the instability of the radical produced by hydrogen abstraction or because of the weak bond between methylene groups. The cleavage step itself probably consumes H_2S. This feature seems worthy of further study, especially as a feature of reversion.

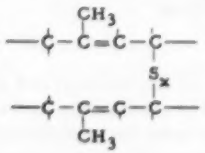
The function of accelerators in vulcanization has been known for at least twenty-five years to be that of converting rings of S_8 to a reactive form. According to the copolymerization theory this active form merely consists of short, suitably terminated open chains (compare Nordlander's ideas which were discussed in Section IV). The shortening of the sulfur chains through the action of H_2S is clearly a reduction and will depend on the following factors which often are interdependent:

1. The concentration (really the activity) of H_2S in the curing system.
2. The concentration of sulfur or polysulfide.
3. The α-methylenic hydrogen activity of polyisoprene.
4. The tendency of polyisoprene chains to cleave between the methylene groups and the tendency of the resulting radicals to participate in reactions with components of the curing system.
5. The polymerization activity of isoprene-unit double bonds with each other and with variously terminated sulfur chains.
6. The acidity and the buffering capacity of the mix. Components of special importance here are ZnO, fatty acid, MBT, amines, water, zinc salts, etc.
7. The presence of H atom supplying compounds, e.g., thiazole thiols or primary and secondary amines, which can also supply groups (amino radicals) for terminating sulfur chains.

The use of S_2Cl_2 as a source of short sulfur chains[117] is attractive. It is now known that this type of vulcanization does not produce insoluble sulfur. The

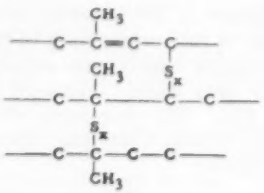
shortpath distillation (at 130° C) of insoluble sulfur-rubber mixes has yielded nearly all the sulfur as a distillate of S_8 without vulcanization of the rubber. Shortpath distillation (also at 130° C) of S_2Cl_2 vulcanizates yielded no sulfur[98] and did not apparently change the vulcanizate. Formerly[92] it had been believed that half of the sulfur in S_2Cl_2 during cure was converted to insoluble sulfur. In the light of the study of Farmer, Ford and Lyons[95] one might expect S_4 crosslinks in this type of vulcanizate.

The copolymerization theory considers that crosslinks should exist in a vulcanizate as copolymer chains of isoprene units and blocks of S_x chains where x = 0, 1, 2, 3, or 4 or rarely more than 4. Wholly disubstitutive, α-methylenic crosslinks, e.g., Formula IV, should exist only infrequently in most vulcanizates.



Formula IV

A structure having Formula V constitutes a chain of crosslinks produced by (1) abstraction of an H atom from a rubber molecule, (2) addition of S_x, (3) addition on the double bond of an isoprene unit of a second rubber molecule, (4) addition of a second S_x, (5) addition of a third isoprene unit, and finally, termination by addition of an H atom. Formula V as a type formula for structures formed early in the cure stage of vulcanization thus illustrates some of the features of the copolymerization theory.



Formula V

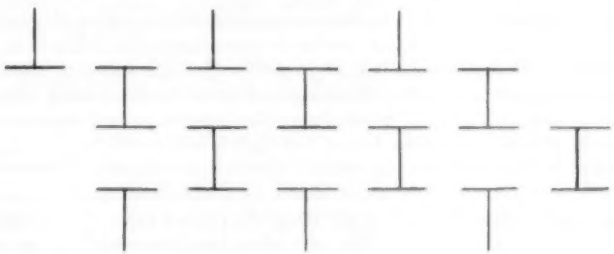
It is purely speculative but is based on polymerization principles and on the findings with regard to vulcanizate structure reported by many workers including Armstrong, Little and Doak, Selker and Kemp, Williams, Bergem, Farmer and coworkers, as well as the recent reports of Glazebrook, Moore and Saville.

The structural feature of Formula V of greatest interest is that the sulfur atoms are situated near each other so that two blocks of sulfur atoms have produced a hexafunctional crosslink. The rubber sulfide theory of Twiss and the colony theory of Kambara[110] also consider a nonrandom distribution of crosslinks. It should be noted for Formula V that two double bonds overall have disappeared with the copolymerization of two blocks of sulfur atoms.

The redistribution of crosslinks is a reaction that is being given considerable attention. A recent article by Krebs[112] reported that alkyl disulfides, though unreactive toward sulfur alone, do react readily with sulfur in the presence of an amine and hydrogen sulfide. Disulfide interchange in polysulfide polymers

was discussed at length by Bertozzi, Davis and Fettes[114], as well as by Tobolsky[115]. The extent of crosslink interchange which occurs during ordinary vulcanization must be appreciable. This is a conclusion that may be drawn from the recent literature. This field, including redistribution of main chain links, is still largely unexplored.

In connection with crosslink and main-link interchange, mention can be made of the finding of McPherson and Bekkedahl[116] that the reaction of rubber with sulfur occurs in two stages. They followed the reaction calorimetrically. The first stage produces, with a large evolution of heat, a product containing 19 per cent sulfur corresponding to 0.5 gram atom of S per C_5H_8 unit. The authors cite other confirmatory evidence. The rubber sulfur reaction eventually tends to produce a reaction product on the average of one sulfur atom per isoprene unit but this second stage reaction evolves only a small amount of heat. We can mention here Barton's recent finding for conditions of optimum crosslinking of one sulfur atom[64] per crosslink. This is compatible with 0.5 sulfur atom per C_5H_8 unit for the first stage of the hard rubber reaction and,



Formula VI

together with other knowledge, suggests Formula VI for an idealized hard rubber of 19 per cent sulfur content. In this formula horizontal bars stand for isoprene units and vertical bars for S_1 crosslinks. Assuming one overall hydrogen transfer for each crosslink half of the double bonds would still be available for the second stage. These would in part simulate the original double bonds in structure as in Formulas IV and V but would have a different reactivity toward sulfur. Some of them in structure and reactivity would be like the double bonds in Formula III. These double bonds remain unreacted during the first stage as a result of α-methylenic hydrogen abstraction and, ultimately, transfer to the other end of the crosslink copolymer chain. In order to produce the structure of Formula VI from that of Formula V it is obvious that crosslink and mainlink scission with various redistribution of the network linkages is needed. These reactions, in the light of recent findings, seem rather plausible.

VII. DEFINITIONS

Vulcanization or cure is an irreversible chemical process during which the ability of an elastomer to flow is reduced and its elastic properties are enhanced. This statement is intended to take into account the pronounced rubberiness of some unvulcanized elastomers and the varying degrees of vulcanization existing in or produced in any particular specimen. Chemically, the process involves the joining of segments of different elastomer molecules so that a network is formed or an existing network extended.

Vulcanizing or curing agents are substances which react with elastomers to produce vulcanizates. The agent, in the case of sulfur and a well-compounded mix, permanently combines with natural rubber with little or no change in the H to C ratio. In the case of peroxides a vulcanizate is produced having a lower hydrogen content than the starting rubber.

Accelerators are substances which increase the rate of reaction of rubber with sulfur and usually, at the same time, the rate of vulcanization. Some vulcanizing agents, depending on the concentration, are also accelerators. For example, 2 phr or more of TMTD in the presence of 5 phr of ZnO vulcanizes NR and 0.2 phr of TMTD accelerates the cure of a NR mix consisting of 5 phr of ZnO, 1 phr of stearic acid and 2 phr of sulfur.

Activators are substances, usually fatty acids or zinc oxide, which increase the effects of accelerators. Of themselves they are neither curing agents nor accelerators.

Retarders are substances which extend the scorch period and usually also the cure period. They often increase the rate and extent of modulus development.

Scorch is a term denoting changes in a mixed stock during the early part of the curing process. The *scorch period* is essentially the induction period of vulcanization. In this review it is identified with chain scission, an effect which makes for easy flow and better molding just prior to the curing stage. Some crosslinking probably occurs throughout the scorch period and may be premature as in processing conducted at too high a temperature.

Reversion is the third and late part of the curing process. It involves weakening of the vulcanizate through crosslink or main-chain scission.

Reclaiming is any process of converting the rubber part of a vulcanizate to a soluble or dispersible form. It, like reversion, involves crosslink or main-chain scission.

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CARBOXYLIC ELASTOMERS

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I. INTRODUCTION

The degree to which a polymer is rubbery is influenced by the detailed shape and chemical composition of the macromolecules[6]. Polymers which are rubbery possess relatively weak interchain forces and may lack linear symmetry and orderly arrangement of the molecule. As stronger interchain forces are added and symmetry and regularity are increased, the rubbery characteristics are gradually supplanted by those of fiber forming materials. Copolymerization with hydrocarbon chains may be used to reduce polymer to polymer interaction, destroy regularity and symmetry and favor rubbery characteristics. On the other hand it may be employed to introduce polar groups into hydrocarbon polymers and thereby increase interchain and intrachain forces. With

increasing amounts of these polar groups polymer strength increases at the expense of elasticity with respect to both speed and range of extension and recovery. The polar groups also alter the solvent resistance of the polymer.

In copolymerizations, carboxylic monomers tend to destroy regularity and symmetry thereby favoring rubbery properties over crystallinity. The strong polar nature of the carboxyl groups however increases interchain and intrachain forces imparting increased strength to the polymer at the expense of elasticity. Carboxyl groups were first introduced into rubbers for the purpose of altering polymer properties[50]. When carboxyl groups are so employed, the resultant carboxylic rubbers are best regarded as polar elastomers.

Carboxyl groups have also been introduced into rubbers in order that reactions characteristic of the carboxylic functional group might be employed to crosslink the polymer chains or attach them to other molecules or surfaces[14,17]. When the carboxyl group is present in order that its functional reactivities may be employed, the carboxylic rubbers are best regarded as functional elastomers.

This review is concerned with the preparation, properties and evaluation of carboxylic rubbers both as polar and as functional elastomers.

II. HISTORICAL BACKGROUND

The first preparation of a carboxylic elastomer was recorded in a French patent[50] published in June 1933. Butadiene was copolymerized with 17.8 phm (parts per hundred of monomer) of acrylic acid in acid emulsion at 60° C. The product was vulcanized in a sulfur recipe accelerated with zinc oxide and dithiocarbamate of decahydroquinaldine using carbon black. The reported vulcanizate properties indicate that this was a typical sulfur cure and no reference was made to recognition of vulcanization properties ascribable to the presence of the carboxyl group.

The copolymerization of butadiene with 15 phm of methacrylic acid in an acid emulsion at 60° C in almost quantitative yields was described in a German patent[60] published in October 1938. No properties of the polymer or its vulcanizates were described.

Copolymerizations of butadiene with methacrylic and with acrylic acid and analogous isoprene copolymers were made in Triton X-30 emulsion for adhesion studies by Frank, Kraus and Haefner[41] in 1952.

The copolymerization of butadiene and its homologs such as isoprene, dimethylbutadiene, and chloroprene with dicarboxylic acids such as maleic acid, fumaric acid, chloromaleic acid, and chlorofumaric acid was reported in a French patent[51] published in June 1939. Details of polymer or vulcanizate properties or methods of vulcanization were not described, but it may be assumed that the vulcanization recipes were based on the action of sulfur.

The preparation of terpolymers and multipolymers containing carboxyl groups was reported[58] in the patent literature in 1946. Dienes such as butadiene, isoprene, 2,3-dimethyl-butadiene, 1,3-pentadiene, and hexadiene-1,3 were copolymerized with a carboxylic monomer such as acrylic acid, methacrylic acid ethacrylic acid or alpha-chloroacrylic acid and a third monomer such as an ester, nitrile or amide of these carboxylic acids. The preparation of butadiene/acrylonitrile/acrylic acid, 55/30/15, and of butadiene/acrylonitrile/methacrylic acid, 55/30/15 gave polymers which, in typical sulfur vulcanizates, showed greater solvent resistance than analogous noncarboxylic polymers.

The polymers were prepared in emulsions based on alkyl benzene sulfonates, sodium lauryl sulfate and similar materials.

The copolymerization of chloroprene in aqueous emulsion with methacrylic acid to give products containing 25 to 80 per cent by weight of methacrylic acid, which were said to resemble vulcanized rubber, has been described in the patent literature[84]. A chloroprene/methacrylic acid copolymer, 70/30 charge ratio, obtained in nearly quantitative yield was described as a clear, dry, tough leatherlike product. No notice was taken of the potentialities of the carboxyl groups in reactions of either the dry polymer or its latex. In a typical polychloroprene gum type vulcanizate with magnesium oxide (10 phr) and zinc oxide (5 phr) the polymer showed a tensile strength of 3430 psi at an ultimate elongation of 430 per cent, properties which were similar to those of a noncarboxylic polymer in such a recipe.

An advertisement[52] of the availability of sorbic acid published in 1946 commented, "The possibilities of extended crosslinkage inherent in its structure make it of great interest in copolymerizations with other olefinic materials". The absence of comment on the potential contribution of this monomer through its carboxyl group of unique properties and reactivities which might make possible crosslinking is noteworthy. This emphasizes the fact that the preparation of rubbers containing carboxyl groups was not recognized at that time as a desirable feature of synthetic elastomers. Actually, sorbic acid copolymerizes with dienes and olefins without imparting significant crosslinking, if any. It has been used to incorporate carboxyl groups[11,15,17].

That thioglycolic acid could be added to pale crepe was reported by Holmberg[46] in 1932. He prepared a product wherein almost one thioglycolic acid unit per each isoprene unit was present. The product was not elastomeric, but a procedure for introducing carboxyl groups had been observed without considering it as such. The reaction has been carried out in benzene with several types of natural rubbers. The reaction was accelerated by oxygen[47]. Some questions concerning the conditions under which thioglycolic acid adds to rubber have been raised by other investigators[29].

The addition of thioglycolic acid to natural rubber, polyisoprene, polybutadiene, and copolymers of butadiene/acrylonitrile, butadiene/styrene and butadiene/α-methyl-p-methylstyrene, in benzene has been described by Serniuk and others[90].

The interaction of maleic anhydride with rubber in solvent in the presence of benzoyl peroxide to form a variety of products ranging from carboxylic elastomeric products to tough, fibrous and even resinous products was described by Bacon, Farmer and others[2,3,35] in 1938. The presence of free carboxyl groups was indicated in each of the several postulated mechanisms of addition of the maleic anhydride to the unsaturation of the rubber molecule. It was postulated that other organic compounds related in their structure to maleic anhydride might be found to add to rubber in a similar manner[2]. The inclusion of other polymerizable vinyls simultaneously with or subsequent to maleic anhydride was proposed, the use of styrene, vinyl acetate and ethyl methacrylate being specifically mentioned[36].

The addition of maleic anhydride to rubber on the mill as well as in solution was described by Compagnon, Le Bras and coworkers[24,25,26] as early as 1941. To products containing maleic anhydride which retained rubbery characteristics the term anhydride rubbers[22,62] was applied. These workers proposed structures for the maleic anhydride reaction products of rubber all of which contained carboxylic and anhydride groups[62].

The patent literature[55] reports the reaction of maleic anhydride and other unsaturated acids with rubber at elevated temperatures without the use of solvent, catalyst, phenol or mixing rolls.

Maleic anhydride rubbers are readily hydrolyzed to carboxylic rubbers[17,56].

The addition of acrylic acid to natural rubber on the mill and in latex has been described by Compagnon and Le Bras[25,26]. That acrylic acid might homopolymerize to give polycarboxylic side chains as well as react with the rubber molecule has been postulated[62]. Acrylic acid is among the monomers reported in the patent literature to add to natural rubber and latex under the influence of a catalyst such as benzoyl peroxide or diazoaminobenzene[61,92,94].

The polymerization of isoprene carboxylic acid, i.e., 2-methyl-1,3-butadiene-4-carboxylic acid, to a "carboxy rubber" by mass, solution and photopolymerization has been described in the literature but the products were not elastomeric[64].

Thus, prior to 1950 the literature reports the preparation of a number of carboxylic rubbers for evaluation as polar elastomers. They were not considered as functional elastomers. Advantage was not taken of chemical reactivity of the carboxyl group for crosslinking. Beginning in 1950 reports of the use of carboxyl groups in rubbers for crosslinking reactions have appeared, thus indicating the consideration of carboxylic rubbers as functional elastomers[9].

III. METHODS OF PREPARATION OF CARBOXYLIC RUBBERS

Prior to 1950 carboxylic rubbers had been prepared either by copolymerization in emulsion of diolefins with acrylic acid type monomers or the addition of a carboxyl bearing molecule, such as thioglycolic acid, maleic anhydride, and acrylic acid to rubber in solvent, on the mill or in latex. With the exception of the copolymerization method these procedures had been applied only to natural rubber.

The preparation of nonelastomeric carboxylic polybutadienes for use as wrapping films by the copolymerization of butadiene with methacrylic acid in cationic or nonionic emulsions was described in 1952 by Miller and Reed[76]. These films were subsequently surface hardened by treatment with metal salt solutions.

That butadiene could not be copolymerized with acrylic acid or with methacrylic acid in the Mutual GR-S polymerization recipe, presumably because the acids were converted to water soluble salts, was observed by Marvel and coworkers[70] in 1952. Polymerization was readily achieved in a recipe acidulated with sulfuric acid. The much greater tendency of methacrylic acid to polymerize in acid than in basic systems has also been reported[7].

Butadiene and isoprene were each copolymerized with acrylic acid and also with methacrylic acid by the use of a Triton X-301 emulsified recipe and potassium persulfate initiation without the addition of mineral acid, acidification being derived from the carboxylic monomers[40,41].

Butadiene was copolymerized with cinnamic acid, with α-cyano-β-phenyl acrylic acid, and with β-(α-furyl)acrylic acid in an acidic recipe with azoisobutyronitrile (Porofor N) initiation by McCain, Marvel and others[67,72]. Copolymers containing 9 to 10.5 per cent of carboxylic comonomer were obtained with cinnamic acid when 10 to 20 per cent comonomer was charged. Cinnamic acid did not homopolymerize. α-Cyano-β-(α-furyl)acrylic acid failed to copolymerize.

Other studies on the copolymerization of butadiene with acrylic acid and with cinnamic acid have been described by R. M. Potts[78] and by C. S. Marvel and coworkers[71]. Recipes employing an alkyl sulfonate, (MP-635-S), an oil-free petroleum sulfonate (Hypanoate L-50), or preferably an acidulated sodium alkyl aryl polyether sulfate (Triton X-301) emulsified system were employed. Porofor N was a commonly employed initiator. In the acidified Triton X-301 system *n*-decyl mercaptan was a preferred modifier but similar results were obtained with *tert*-dodecyl mercaptan[78].

β-2-Thienylacrylic acid was copolymerized with butadiene, and with isoprene in an acidic recipe initiated with azoisobutyronitrile. Attempts to similarly prepare a copolymer with ethyl acrylate were unsuccessful[72].

The polymerization of butadiene with acrylic acid and with methacrylic acid in recipes emulsified with Triton 773 or X-301 without the addition of acidulating agents other than the carboxylic monomers has been described by Frank and Kraus[39]. Potassium persulfate initiation with dodecyl mercaptan or tert-octyl mercaptan modification was employed. Unmodified polymers were also prepared. Terpolymers of butadiene, styrene and methacrylic acid were also mentioned. Miller and Reid[76] employed Arctic Syntex M as the emulsifier for butadiene copolymerization with methacrylic acid.

The preparation of copolymers of butadiene with sorbic acid, butadiene with vinylacrylic acid, butadiene with styrene and sorbic acid, butadiene with acrylonitrile and sorbic acid and similar monomer combinations involving acrylic acid type monomers in polymerization systems emulsified with dodecylamine hydrochloride or similar acidic emulsifiers, Nacconol NRSF with Triton X-100, and also in an emulsifier-free system was described by Brown[15].

The preparation of a butadiene, acrylonitrile, sorbic acid terpolymer initially charged 70/25/5 in an Aquarex D emulsified recipe initiated with sodium perborate has been described in the patent literature[22]. The carboxyl content of the polymer was not reported. It is known that sorbic acid enters the polymer at less than the charged level and since the reported conversion was 59.7 per cent the incorporation was probably less than 5 per cent.

The preparation of terpolymers of butadiene, acrylonitrile and acrylic acid has been described by C. S. Marvel and coworkers[71]. A sodium alkane sulfonate emulsified system was employed with azoisobutyronitrile (Porofor N) as the initiator and a mixture of straight chain mercaptans (about C_{12}) as the modifier agent.

Carboxylic elastomers have been prepared from unsaturated synthetic elastomers by treatment in solvent with maleic anhydride in the presence of a catalyst such as benzoyl peroxide[10,17].

The preparation of a carboxylic polymer from a butadiene/acrylonitrile copolymer by treatment with maleic anhydride in an internal or Banbury mixer has been mentioned in the adhesives patent literature[28]. Thus a butadiene copolymer containing 35 per cent acrylonitrile was treated with 5 per cent of maleic anhydride at 205° to 210° F.

The carboxylation of vulcanized natural rubber and butadiene/styrene copolymers by treatment with maleic anhydride in an extruder plasticator has been described by Green and Sverdrup. Other unsaturated carboxylic acids may be similarly employed. Compounds which can liberate unsaturated acids when heated may be employed. Thus citric acid which yields aconitic acid has been used[42].

The treatment of butadiene/acrylonitrile copolymers with 5 or 10 parts of maleic anhydride on the mill by the method of Compagnon and Bonnet to

produce anhydride rubbers for reaction with epoxy resins has been mentioned by T. K. Mika[74].

The preparation of carboxylic products from polybutadiene, polyisoprene, and butadiene/styrene copolymers by treatment of hydrocarbon solutions of the polymers with thioglycolic acid has been described in the patent literature[39]. Other mercapto acids and especially β-mercapto propionic acid have been employed with a variety of unsaturated polymers in solvent or dispersions with peroxidic catalysts to produce carboxylic elastomers[10,17].

Methacrylic acid was one of a group of monomers reported to have been incorporated "by swelling into natural rubber, and under more restrictive conditions into synthetic rubbers, and then applying shear" by L. C. Bateman[5]. No properties or reactions of the carboxylic rubbers were described.

Anhydride synthetic rubbers have been prepared by copolymerizations with maleic anhydride or itaconic anhydride or similar monomers in solvent. Thus ethyl acrylate and maleic anhydride have been copolymerized in methyl ethyl ketone[19].

The preparations of carboxylic rubbers for the specific purpose of subsequent reactions, especially crosslinking reactions have employed the following methods[17]. Unsaturated carboxylic acids of the acrylic acid type have been copolymerized with dienes and olefins in emulsion, in solvent and in bulk[11,21]. Carboxyl-bearing molecules reactable with unsaturated polymers have been added to elastomers on the mill, in solvent and in latex[10]. Molecules containing groups convertible to carboxyl groups have been similarly added and subsequently converted to carboxylic rubbers.

Carboxylic rubbers have been prepared from latices of polyethylacrylate, butadiene/ethyl acrylate, butadiene/methyl methacrylate and butadiene/acrylonitrile copolymers. Such latices may be made in alkaline emulsion systems employing common anionic soaps[16,17].

The preparation of a carboxylic polyisobutylene by the copolymerization of acrylyl chloride with isobutylene and subsequent hydrolysis of the acid chloride has been described[12].

For the copolymerization of carboxylic monomers of the acrylic acid type into rubbers an acid-type recipe is essential. Acidity, if not a characteristic of the emulsifier, may be derived from the addition of mineral acids or in some instances the acidic character of the carboxylic monomers may be ample. Acrylic acid, methacrylic acid and sorbic acid have been copolymerized with many olefins and diolefins such as the acrylic and methacrylic acid esters, styrene, acrylonitrile, methacrylonitrile, vinylidene chloride, butadiene, isoprene, 2,3-dimethylbutadiene, and chloroprene. Other carboxylic monomers have included β-acryloxypropionic acid, ethacrylic acid, 2-ethyl-3-propylacrylic acid, itaconic acid, cinnamic acid, vinylacrylic acid, maleic acid, and fumaric acid. Several terpolymer systems have yielded interesting rubbers such as carboxylic copolymers of butadiene/styrene, butadiene/acrylonitrile, butadiene/acrylate esters, butadiene/vinylidene chloride or butadiene/methacrylonitrile[17].

The amount and distribution of carboxyl groups of polymers prepared in emulsion systems have been controlled by the choice of the comonomer, acids the monomer charging ratio, the conversion, the proportioning of one or more monomers, and the use of mixtures of acrylic-type acids[17]. In some instances the temperature of polymerization has significant influence on polymer quality. Many emulsifying agents have been investigated for the preparation of carboxylic rubbers but the essential feature is an acidic recipe[17,19,39,67,71,72,75,76,7 ar-

IV. PROPERTIES OF UNVULCANIZED CARBOXYLIC RUBBERS

The influence of the incorporation of carboxyl groups upon the properties of elastomeric hydrocarbon polymers was first reported by Farmer and others in their comments upon the influence of the addition of maleic anhydride upon the properties of rubber[2]. They found that the incorporation of a very little maleic anhydride gave very considerable modification in the physical properties of rubber. Toughening and loss of tack increased with the incorporation of increasing amounts of maleic anhydride. Products ranging from elastic rubber-like materials through fibrous substances to brittle resins were prepared[26]. Reaction of the rubber-maleic anhydride products with reagents which might be expected to attack the anhydride groupings such as aniline, alcohols and caustic alkalies was postulated[27]. Thermoplastic or resinous products were obtained by treating the rubber and maleic anhydride products with glycols or diamines[32]. Reaction of the maleic anhydride rubber with other polymers containing groups reactable with the anhydride linkage such as the hydroxyl groups of cellulose acetate was also mentioned by Farmer[34]. Ethers as well as esters of cellulose were reacted with the maleic anhydride rubber in a suitable solvent such as acetone[32].

The anhydride rubbers have been described as resembling at the same time both crude rubber and vulcanized rubber. Maleic anhydride is an effective stiffening agent for rubber. The anhydride rubbers may be vulcanized with sulfur[22,32].

In rubbers treated with maleic anhydride, the more maleic anhydride present the greater the reduction in thermoplasticity which occurs from the action of an agent such as benzene sulfonic acid. However, this improvement is offset by the fact that the more maleic anhydride the less soluble the products and the poorer their adhesion to metal[52].

The addition of thioglycolic acid to polybutadiene, polyisoprene, or butadiene/styrene copolymers rendered these polymers increasingly resistant to hydrocarbon solvents as the amount of thioglycolic acid was increased[39].

The incorporation of increasing amounts of acrylic acid into natural rubber caused progressive decrease in solubility in hydrocarbon solvents[25]. The products were harder and had lower elongations than the untreated rubber. The incorporation of acrylic acid was less satisfactory than that of maleic anhydride because of its volatility. Itaconic acid, crotonic acid and citraconic anhydride were also added to rubber[62].

The copolymerization of increasing amounts of methacrylic acid with butadiene yielded polymers which were progressively more inelastic or less rubbery. Elasticity was gone at 40 to 45 per cent methacrylic acid[41,76]. In general the inclusion of increasing amounts of carboxyl in an elastomer elevated the temperature range of elasticity[17]. Millability decreased with increasing carboxyl content[41]. Solubility in rubber solvents decreased with increasing carboxyl content. Cyclohexanone and dioxane are good solvents for butadiene/methacrylic acid copolymers. Films cast from the copolymer latices varied from hard and celluloid-like for a 40/60 butadiene/methacrylic composition to soft and extensible for an 80/20 composition[41].

The inclusion of increasing amounts of carboxyl groups in polyacrylates by copolymerization with acrylic and methacrylic acids made the polymers increasingly tougher and harder to handle[21]. The stiffening effect of carboxyl groups upon methyl acrylate and ethyl acrylate polymers was noted by Semegen and Wakelin[67]. Copolymers prepared with monomer charges containing

ten percent acrylic acid were observed to be stiffer than non-carboxylic polymers.

In general, the inclusion of carboxyl groups in any rubber molecule by means of the copolymerization of an acrylic type acid such as acrylic acid or methacrylic acid has the following effects[17]. With increasing carboxyl levels the elasticity range is elevated, film forming tendencies are enhanced, resistance to hydrocarbon solvents is increased, centers for crosslinking by polyvalent and especially divalent reagents are introduced, hardness and abrasion resistance are increased, and adhesion to many surfaces and especially metals is improved. The carboxyl groups confer alkali or ammonia sensitivity which becomes a significant tendency for solubility for low molecular weight high carboxyl content polymers[20].

The physical properties of a carboxylic rubber having a carboxyl content of 0.1 equivalent per hundred grams of rubber or less are essentially those of an analogous noncarboxylic polymer. The usual influences of modification upon polymer plasticity, gel content and molecular weight have been observed. Pigments are more readily incorporated into low Mooney viscosity polymers of low gel content than into higher viscosity high gel polymers[14].

The suggestion[4] that the introduction of a few carboxyl groups (one carboxyl to 200 carbon atoms) into butadiene/acrylonitrile rubbers can convert them into rubbers which will resist even chlorinated solvents seems overly optimistic.

Carboxyl groups incorporated into vulcanized scrap natural rubber or butadiene/styrene copolymers by mastication with maleic anhydride conferred upon these materials a degree of oil resistance, a property not normally observed in a tire reclaim[42].

There is evidence that the carboxylic groups may make rubbers more susceptible to oxidative attack[19,66]. Frank, Kraus and Haefner observed that unmodified butadiene/methacrylic acid copolymers undergo relatively rapid oxidative attack, suggesting a catalytic effect of the acid groups[41]. The oxidative attack may cause both degradation and crosslinking. Isoprene/methacrylic acid copolymers were more subject to autooxidative degradation than butadiene/methacrylic acid copolymers. Similarly with polyisoprene, oxidative degradation predominates whereas with polybutadiene crosslinking predominates. Basic materials such as *p*-hydroxydiphenylamine, *m*-phenylenediamine, and the mono, di and tri ethanol amines were retarders of oxidative attack but also tended to retard cure and reduce adhesive properties[41].

V. DETERMINATION OF CARBOXYL CONTENT OF CARBOXYLIC RUBBERS

The estimation of carboxyl content of carboxylic polymers by C. S. Marvel and coworkers was based upon carbon and hydrogen analyses, and the titration of unpolymerized entrapped acid monomer of the polymerization aystem[78].

A method for the determination of carboxyl content of maleic anhydride adducts of vulcanized natural rubber or of butadiene/styrene copolymers has been described by Green and Svedrup[42]. The polymer was allowed to stand with excess alkali overnight. Titration of the unused alkali by acid gave a measure of the carboxyl content of the polymer.

The carboxyl content of many carboxylic elastomers has been determined by titration with alcoholic alkali in appropriate solvents. Pyridine has been successfully employed with almost all carboxylic rubbers. Erratic results may

be obtained if polymers are poorly soluble or gel forms during titration. The reliability of the method was verified by carbon and hydrogen analyses of selected polymers. It was also verified by determining the amount of palmitic acid which could be volatilized after treating a selected polymer with an excess of zinc palmitate[17].

VI. CARBOXYLIC RUBBERS AS RAW MATERIALS

Carboxylic rubbers may be used as raw materials for the synthesis of other polymers, resins and even chemicals. The potentialities of carboxylic rubbers from maleic anhydride and rubber for the preparation of a variety products of technical interest by further reactions of the carboxyl anhydride groups was suggested by Bacon, Farmer and coworkers[3]. Reaction of maleic anhydride rubber with glycols or diamines to give resins has been described[32,34].

Resins were obtained by Redfarn and Schidrowitz by treating rubber with maleic anhydride and a phenol and then subsequently with an adlehyde such as formaldehyde for which they described values in the formulation of molding compositions[79,80,81].

Adhesive compositions resistant to mineral oils have been reported in the patent literature to result from the treatment of crepe rubber with maleic anhydride in benzene together with ethanol in the presence of a catalyst such as benzoyl peroxide[83].

Carboxylic rubbers have been converted into elastomeric polymers containing acid chloride groups by treatment with oxalyl chloride and the products subsequently reacted with alcohols and amines[19].

The use of carboxylic rubbers as raw materials for organic synthesis has received too limited attention.

VII. VULCANIZATION OF CARBOXYLIC RUBBERS

A. SULFUR VULCANIZATION OF CARBOXYLIC RUBBERS

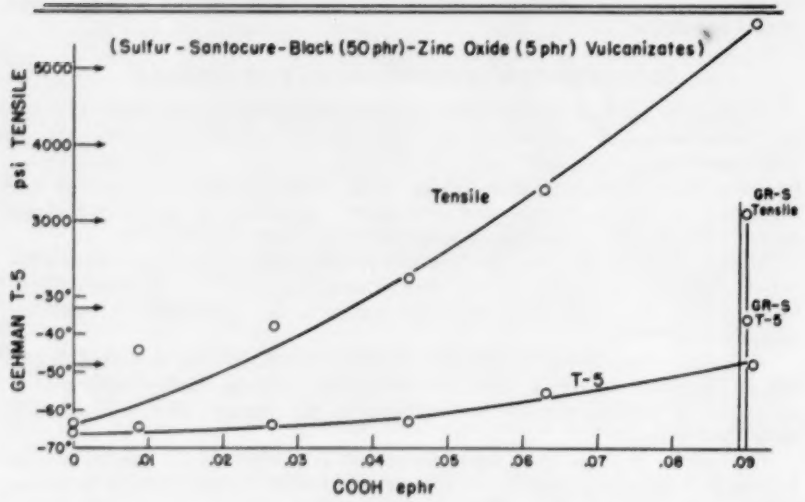
Carboxylic rubbers have been vulcanized in the sulfur type vulcanization recipes commonly employed for the vulcanization of analogous noncarboxylic rubbers. This has been true of carboxylated natural rubber[23]. It has been equally true of carboxylated synthetic rubbers and of carboxylic rubbers prepared by copolymerization[17,67,70,72].

In recipes containing both metal oxide and sulfur vulcanizing agents there are competing vulcanization reactions between metallocarboxylate formation and the sulfur vulcanization. Thus, in a zinc oxide accelerated sulfur vulcanization with bis(dimethylthiocarbamyl) disulfide (TMTD) the zinc oxide reaction is very fast, a high tensile strength resulting in relatively short curing times. With longer curing cycles the slower sulfur cure takes over and the tensile drops. Vulcanizate properties dependent on stress relaxation are poor for those cures in which the action of zinc oxide predominates. As the sulfur cure takes over the compression set and related properties improve and the tensile drops. Similar observations have been made on recipes employing zinc oxide with sulfur and zinc dimethyldithoicarbamate (ZnDMDC), bis(dimethylthiocarbamyl) monosulfide (TMTM), 2,2′-dithiobisbenzothiazole (MBTS), N-cyclohexyl-2-benzothiazole sulfenamide (CHBS), and similar cure systems. The higher the carboxyl content of the polymer the more noticeable the effect. See Table I and Figure 1[17,65].

Stress-strain data reported in Tables I and III and Figures 1 to 9 inclusive

FIG. 1.

DEPENDENCE TENSILE and GEHMAN VALUES of BUTADIENE–SORBIC ACID COPOLYMERS on CARBOXYL CONTENT



were determined on 0.025 inch thick tensile sheets (i.e., microtensile sheets) which give tensile values of the order of 20 percent higher than are obtained with regular ASTM sheets which are 0.075 inch in thickness. The standard rate of pull, 20 inches per minute was employed.

TABLE I

INFLUENCE OF CARBOXYL LEVEL UPON DOMINANCE OF METALLOCARBOXYLATE OVER SULFUR CURE[a]

Cure, min at 300° F		Carboxyl content (ephr)[b] 0	0.02	0.08	0.18
10	300% Modulus, psi	<100	760	900	2300
	Tensile, psi	1630	5300	4690	6080
	Elongation, %	880	700	595	450
20	300% Modulus, psi	200	700	1350	3000
	Tensile, psi	2850	3650	5000	6090
	Elongation, %	860	595	540	380
40	300% Modulus, psi	310	1000	1590	3320
	Tensile, psi	3490	3060	2950	4200
	Elongation, %	795	540	460	365
80	300% Modulus, psi	460	1110	1830	4390
	Tensile, psi	2400	1600	2850	5090
	Elongation, %	700	380	395	395
40	20% Stress loss time, hours	1.0	0.56	0.07	0.03

[a] Data from Reference 19. Vulcanizate recipe per hundred grams of polymer: Zinc oxide 5, MBTS 1.25, Cumar softener 5, and Sulfur 1.25.

[b] Butadiene/acrylonitrile copolymer with acrylonitrile, Hycar 1001 type. Carboxyl expressed in equivalents per 100 g. of rubber.

A very light sulfur cure is often desirable to improve the poor permanent set properties of metallocarboxylate vulcanizates but this always has an adverse effect on tensile, tear and related properties[17,75].

In the vulcanization of anhydride rubbers with sulfur Compagnon and Bonnet[22] suggested that the presence of uncombined maleic anhydride might account for the poor stress strain properties observed, which they interpreted as due to an under cure. The possibility that combined maleic anhydride might also have a retarding effect was recognized. Therefore they added polyhydroxy compounds, especially ethylene glycol to neutralize the free anhydride and carboxyl groups. Best results were obtained by the use of bases both inorganic and organic in amounts sufficient to neutralize the maleic anhydride. Hexamethylene tetramine was considered an excellent additive which contributed a plasticizing as well as a neutralizing action. With increasing levels of maleic anhydride the sulfur vulcanizates showed increasing modulus and decreasing elongation values. Swell in gasoline was reduced, as well as thermoplasticity and permeability to gases. The serious disadvantage of these polymers was their poor flex life and poor resistance to tear. Thus, with these vulcanizates it is evident that metal oxide and sulfur vulcanization were competing. Probably the ethylene glycol formed ester crosslinks and the diamines formed salt and amide crosslinks.

Similar speculations that in carboxylic elastomer sulfur vulcanizates the presence of unneutralized carboxyl groups (or of —COOZnOH groups when zinc oxide was present) might be responsible for inferior properties had led to the inclusion of organic amines, and weak acids in sulfur vulcanization recipes with some improvement of vulcanizate properties[19].

Carboxylic polybutadienes were evaluated by Marvel, Taft and coworkers in a recipe employing EPC black (40 phr) zinc oxide (5 phr), sulfur (2 phr), and MBTS (1.75 phr). Evidence of reaction of the carboxyl group in this vulcanization was not noted but can be observed in the data[70]. That the low temperature properties of a butadiene copolymer with 10 per cent methacrylic acid were inferior and the oil resistance superior to those of a butadiene copolymer with 10 per cent acrylic acid verified the fact that methacrylic acid copolymerizes more readily than acrylic acid with butadiene.

A carboxylic polybutadiene containing 9.6 per cent cinnamic acid was evaluated in the recipe of the preceding paragraph. A tensile strength of about 5370 psi, a Gehman T-5 value of $-61.5°$ C, and oil resistance inferior to, and hysteresis about equal to, that for a butadiene/styrene copolymer (SBR) was reported by McCain and others[67,72]. No observation of possible participation of the carboxyl group in the cure was mentioned. However, the fact that the highest tensile strength was observed at the lowest cure and the lowest tensile (3690 psi) at the longest cure indicates predominance of the zinc salt cure in the first stages of vulcanization followed by gradual displacement by the sulfur cure with increased cure times. Similar evaluations were made with the recipe Statex 93 black (30 phr), red lead (2.5 phr), Circosol 2XH (20 phr), sulfur (2 phr) and MBTS (1 phr) and the influence of the carboxyl groups was indicated by the elevated moduli and reduced elongations of the carboxylic polymer compared with the control SBR polymer[72].

The influence of carboxyl groups on a tread type recipe based on sulfur (1.5 phr), black (50 phr), CHBS (1.25 phr) and zinc oxide (5 phr) is well illustrated by a series of butadiene/sorbic acid copolymers of comparable conversion (ca. 75 per cent). Tensiles increased from less than 500 psi for no sorbic acid to 5500 psi for 0.09 equivalent of sorbic acid per hundred of rubber.

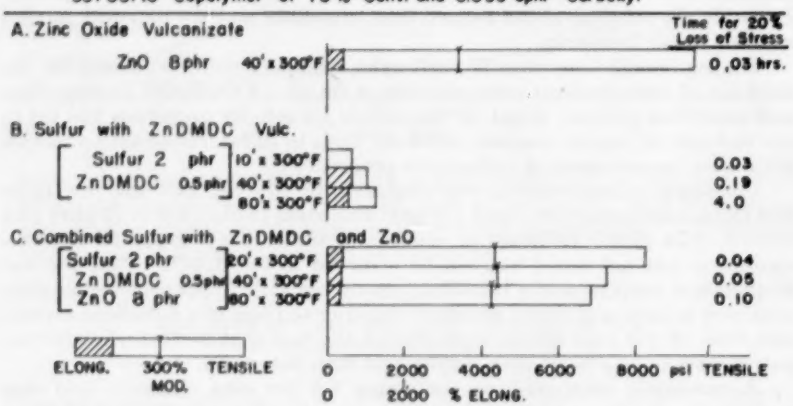
Low temperature Gehman T-5 values[8] rose from −65° C to −46° C. See Figure 1.

The vulcanization of butadiene terpolymers containing acrylonitrile and acrylic acid of 50 to 56 per cent conversion containing 0.025 to 0.06 ephr of carboxyl in an MBTS (1.75 phr), sulfur (2 phr) zinc oxide (5 phr), EPC black (40 phr) tread type recipe and in an MBTS (1 phr), sulfur (2 phr), red lead (2.5 phr), Statex 93 black (30 phr), Circosol 2XH (20 phr) carcass type recipe has been described by C. S. Marvel and coworkers[71]. No mention was made of the influence of the carboxyl groups of the polymer upon the zinc oxide and lead oxide of these recipes. The polymers were stated to possess better oil resistance than GR-S but not to be equal to Perbunan 18. Inspection of the stress-strain and stress-relaxation data indicate the competition of the metal oxide and sulfur vulcanization reactions.

FIG. 2.

SEPARATE and COMBINED ZINC OXIDE and SULFUR VULCANIZATES of a BUTADIENE / ACRYLONITRILE / METHACRYLIC ACID

55/35/10 Copolymer of 73 % Conv. and 0.099 ephr Carboxyl



It is possible to cure carboxylic rubbers in sulfur recipes containing no metal oxides and observe that for polymers containing less than 0.1 ephr of carboxyl the vulcanizate properties are essentially identical with those of similar vulcanizates of noncarboxylic analogs. Vulcanization of carboxylic rubbers with metal oxides may be superimposed upon sulfur vulcanization. Also sulfur vulcanization may be superimposed[17] upon metal oxide vulcanization. In these cases, as is also true when the two vulcanizations are carried out simultaneously, a compromise of properties results in all cases, wherein the tensiles are higher and the properties related to compression set poorer with increased predominance of the metal oxide vulcanization. See Figure 2.

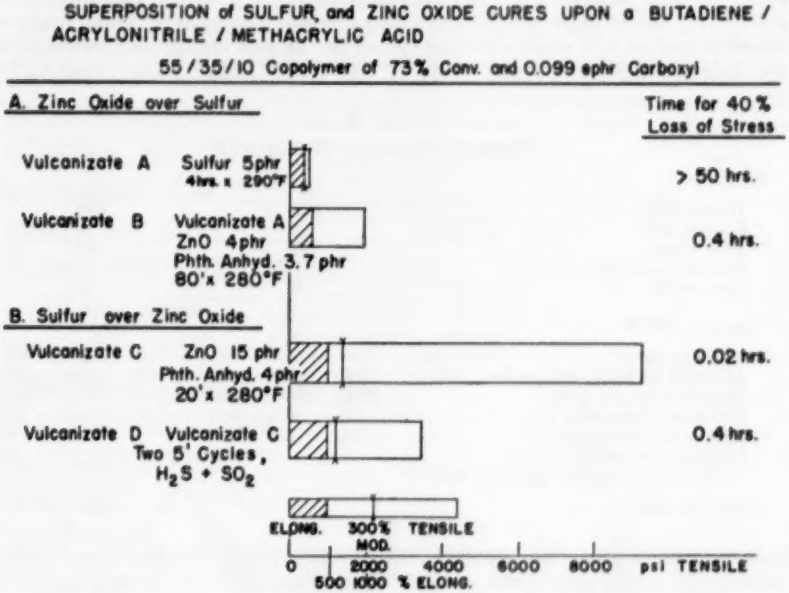
Superposition of a sulfur cure upon a zinc oxide cure has been illustrated with a carboxylic butadiene/acrylonitrile copolymer having a carboxyl content of 0.1 equivalent per hundred grams of rubber. Vulcanized with zinc oxide (10 phr) and phthalic anhydride it showed a tensile strength of 7800 psi at 475 per cent ultimate elongation. This vulcanizate was subjected to a Peachy type cure (two five minute cycles of SO_2 and H_2S) and the tensile strength dropped

to 2420 psi at 395 per cent ultimate elongation[19]. Compare also the data of Figure 3.

B. PEROXIDE VULCANIZATION OF CARBOXYLIC RUBBERS

Carboxyl groups have little or no influence on the vulcanization of unsaturated elastomers with organic peroxides. Thus a carboxylic butadiene/acrylonitrile copolymer (Hycar 1072) when compared with its noncarboxylic analog (Hycar 1042) in a recipe consisting of FEF black (40 phr), stearic acid (1 phr) and dicumyl peroxide (1.75 phr) exhibited virtually identical vulcanizate properties[49].

FIG. 3.



The curing of cements of butadiene/methacrylic acid copolymers with cumene hydroperoxide, lauryl peroxide, *tert*-butyl hydroperoxide, cyclohexanone peroxide, methyl ethyl ketone peroxide and hydrogen peroxide was reported by Frank, Kraus and Haefner[41]. They preferred cumene hydroperoxide. There was evidence that the copolymers sometimes contained sufficient residual peroxide from the polymerization reaction to be "self-curing".

Peroxide cures, for example with dicumyl peroxide, may be used in conjunction with metallocarboxylate vulcanization to reduce permanent set. In some respects it is preferable to sulfur vulcanization for this purpose, having a less deleterious effect on tensile. Metallocarboxylate cure occurs first, the peroxide cure requiring more severe cure cycles[19,49,65,75] (Table II). Tertiary butyl hydroperoxide has been similarly employed but is less satisfactory than dicumyl peroxide because of its greater volatility. Peroxide cures have also been employed in conjunction with hexamethylene diamine carbonate vulcanization of carboxylic rubbers, especially polyacrylates to improve compression sets and

related properties. Benzoyl peroxide has been similarly employed but is not as satisfactory as dicumyl peroxide[19].

C. METAL SALT VULCANIZATION OF CARBOXYLIC RUBBERS

Carboxylic rubbers have been crosslinked by reactions characteristic of the carboxyl groups as well as by the usual sulfur and other methods of vulcanization applicable to analogous noncarboxylic polymers[14]. The reactions of the carboxyl group which have been employed for crosslinking have included salt formation, reaction with diepoxides or poly epoxides including epoxy resins, esterification with polyhydric alcohols, amide formation with poly amines, and anhydride formation[17]. The simplest of these reactions and one of the most extensively studied has been that of salt formation with a metal oxide, hydroxide, or salt of an acid weaker than acetic acid or an acid readily eliminated from the vulcanization site. Salts of Zn^{++}, Ca^{++}, Pb^{++}, Mg^{++}, Cd^{++} and Al^{+++}

TABLE II

PEROXIDE CURES OF HYCAR 1072[a]

Recipe						
Hycar 1072	100			100		
Stearic acid	1			1		
FEF black	40			40		
Dicumyl peroxide	1.75			1.75		
Zinc oxide	0			5		
Cures at 310° F						
Minutes cured	15	30	45	15	30	45
Modulus at 100% elongation (psi)	360	255	360	750	1320	1875
Tensile strength (psi)	2805	2550	2875	3525	4470	4610
Ultimate elongation (%)	430	390	400	320	320	250
Hardness (Durometer A)	65	65	67	78	85	87
Compression set—(%)			25			35
ASTM Method B, 70 hrs at 212° F						

[a] From Reference 65.

have been especially considered[10,18]. However, vulcanization has been demonstrated with many polyvalent metals. Organo-metallic radicals such as found in dibutyl tin oxide have been employed[18]. Calcium silicate, sodium aluminate, and sodium phosphoaluminate have been mentioned as curing agents for carboxylic butadiene/acrylonitrile copolymers[19,65]. Other metal salts[19] or metal alkoxides used to develop metallocarboxylate vulcanizates (Figure 4) have included calcium sulfide, calcium salt of pentanedione, aluminum isopropylate, calcium hypochlorite, zinc catecholate, lead dioxide, methyl zimate, barium oxide, zinc salt of 2-mercaptothiazoline, zinc xylylmercaptide, zinc salt of 2-mercaptothiazole, the monohydrated tribasic lead salt of maleic acid, basic zinc maleate, beryllium oxide, zinc carbonate, and zinc acetate.

Metals as well as their salts have been used to crosslink carboxylic rubbers. Thus, finely divided magnesium has been used with carboxylic polybutadiene and with carboxylic polyethyl acrylates. However, microscopic pieces of unreacted metal not consumed in crosslinking reactions create regions around which failures occur rendering the vulcanizates unsatisfactory[19].

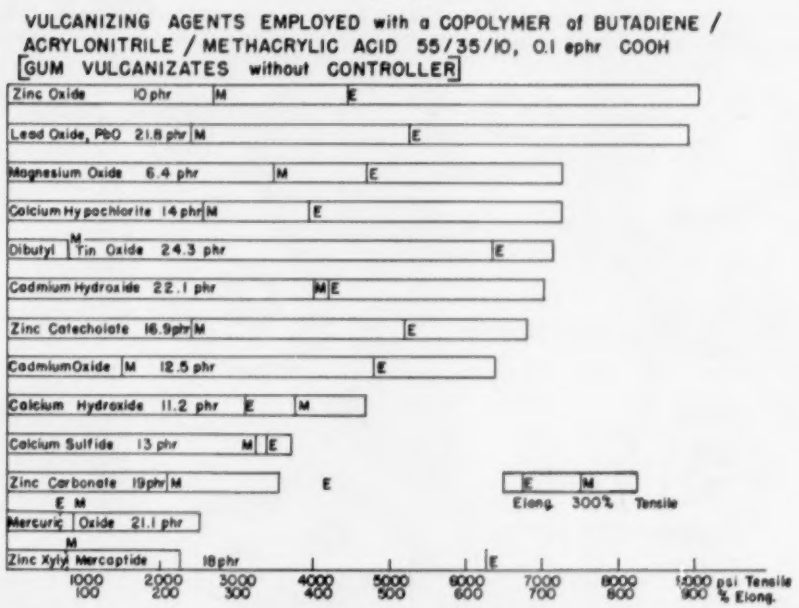
Metal alkoxides such as aluminum isopropylate will also crosslink carboxylic rubbers. The alkoxides are hydrocarbon soluble and may be predispersed in

liquid rubber or solvents to facilitate incorporation with a minimum of milling[19].

Either free carboxyl or monovalent salts of carboxyl groups in polymers may react with polyvalent metals and their salts to give metallocarboxylate vulcanizates, but the free carboxyl groups are more reactive[17,19,75].

The temperature reached during mill incorporation of zinc oxide or other metallocarboxylate crosslinking agents into carboxylic rubbers and the scorchiness of such stocks has been reduced by the use of very finely divided dispersions in a minimum of plasticizing agents. Liquid or soft rubbers including carboxylic rubbers have been used as dispersion and plasticizing media for metal salts[19].

FIG. 4.


VULCANIZING AGENTS EMPLOYED with a COPOLYMER of BUTADIENE / ACRYLONITRILE / METHACRYLIC ACID 55/35/10, 0.1 ephr COOH
GUM VULCANIZATES without CONTROLLER
Zinc Oxide 10 phr
Lead Oxide, PbO 21.8 phr
Magnesium Oxide 6.4 phr
Calcium Hypochlorite 14 phr
Dibutyl Tin Oxide 24.3 phr
Cadmium Hydroxide 22.1 phr
Zinc Catecholate 16.9phr
Cadmium Oxide 12.5 phr
Calcium Hydroxide 11.2 phr
Calcium Sulfide 13 phr
Zinc Carbonate 19phr
Mercuric Oxide 21.1 phr
Zinc Xylyl Mercaptide 18phr
M
E
Elong.
300%
Tensile
1000 2000 3000 4000 5000 6000 7000 8000 1000 psi Tensile
100 200 300 400 500 600 700 800 900 % Elong.

When films of carboxylic rubbers or their monovalent salts are suspended in or washed with solutions of divalent salts a formation of metallo carboxylate crosslinks may occur with divalent salts of even strong acids. Thus a carboxylic butadiene/acrylonitrile copolymer suspended in calcium nitrate or calcium chloride solution will form the calcium vulcanizate[14,19].

The observation that acetone-benzene solutions of maleic anhydride cyclized rubber were gelled when treated with alkaline hydroxides and salts or with alkaline earth oxides or carbonates indicates that such agents cause more or less crosslinking of this type of carboxylic rubber[77].

The hardening of inelastic films of copolymers of butadiene and methacrylic acid by treatment with salts of polyvalent metals represents a crosslinking of polymer chains of the surface by metal salt formation[76]. The adhesion of copolymers of butadiene and methacrylic acid copolymers to metal surfaces probably is due to reaction of the carboxyl groups with the metal surface[41]. That the adhesion may be further enhanced by the use of an intermediate coat of

flocculated carbon cement has been interpreted by the discoverers, G. M. Sheehan, G. Kraus and A. B. Corciation[91], as due to hydrogen bonding between carboxyl groups of the copolymer and oxygen containing functional groups on the carbon surface.

The vulcanization of polyacrylate rubbers by potassium hydroxide, sodium metasilicate, lead oxide and other bases has been interpreted as being due to a Claisen type condensation by Semegen and Wakelin[87]. They demonstrated the formation of ethanol in the vulcanization of polyethyl acrylate. They suggested that their observations as well as their studies on a copolymer of methyl acrylate and acrylic acid might also be interpreted as due to a cure resulting from side chain association through hydrogen bonding. In the case of lead oxide they suggested that primary bonds might be formed between this reagent and the carboxyl groups, but speculated that compounds vulcanized by

TABLE III

INFLUENCE OF SODIUM SALT FORMATION ON STRESS–STRAIN PROPERTIES OF A BUTADIENE/METHACRYLIC ACID COPOLYMER[a]

	Tensile, psi	Elongation, %
Raw Polymer		
84% conversion		
0.118 ephr COOH	<100	>1600
Treatment A		
0.12 ephr of aqueous NaOH (2N)		
Added on mill		
Molded 20 min at 270° F (smooth, opaque)	1700	900
Treatment B		
0.12 ephr of NaOH in EtOH		
Added to polymer in EtOH solution		
Molded 10 min at 360° F (rough, clear)	1000	155
[0.12 ephr ZnO]	[6000]	[400]

[a] From Reference 8.

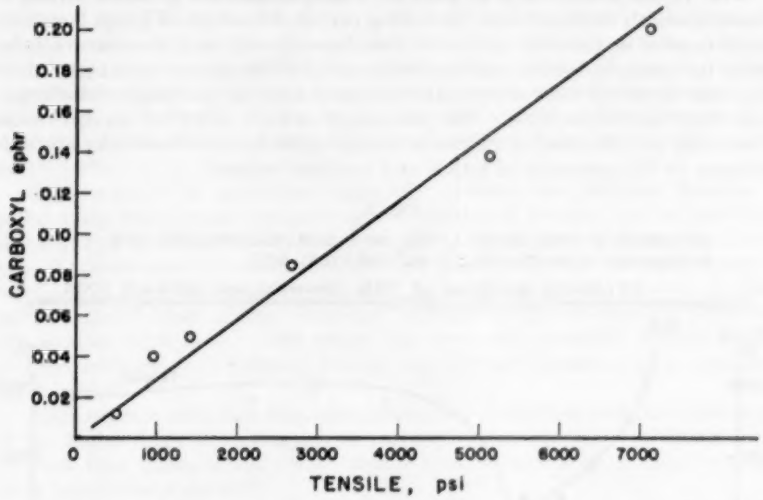
hydrolysis alone would be unstable against high humidity aging. This latter interpretation would represent a case of a metallocarboxylate vulcanization of a carboxylic rubber. Subsequently others have found that metal salt vulcanizates of carboxylic polyacrylates are quite stable toward moisture and even alkalies[17,21]. The uniqueness of litharge as a hydrolyzing agent for esters has been noted with esters of drying oils as well as with the polyacryates. (Compare Chatfield, H. W., The Oil and Color Trades Journal **98**, 66 (July 12, 1940).)

Carboxyl groups of themselves can impart an increase in tensile strength suggestive of crosslinking. In butadiene/methacrylic acid copolymers when there was less than 0.1 of an equivalent of carboxyl per hundred grams of polymer the raw polymer had ultimate tensiles of less than 100 psi. But when the carboxyl content was increased to 0.377 equivalent the molded raw polymer showed a tensile strength of 3000 psi at 365 per cent ultimate elongation[17]. When the carboxyl content was 0.54 equivalent (i.e., 46 per cent methacrylic acid in the polymer) molded raw polymer showed a tensile strength of 8740 psi and 25 per cent elongation[8].

Monovalent ions enhance this chainlinking influence of the carboxyl groups, imparting a degree of "cure" to the polymer. Thus, a butadiene/methacrylic

FIG. 5.

VULCANIZATION of COPOLYMERS of BUTADIENE – ACRYLIC TYPE ACID (90%+ CONVERSION) COPOLYMERS with EXCESS ZINC OXIDE. INFLUENCE of CARBOXYL LEVEL UPON TENSILE

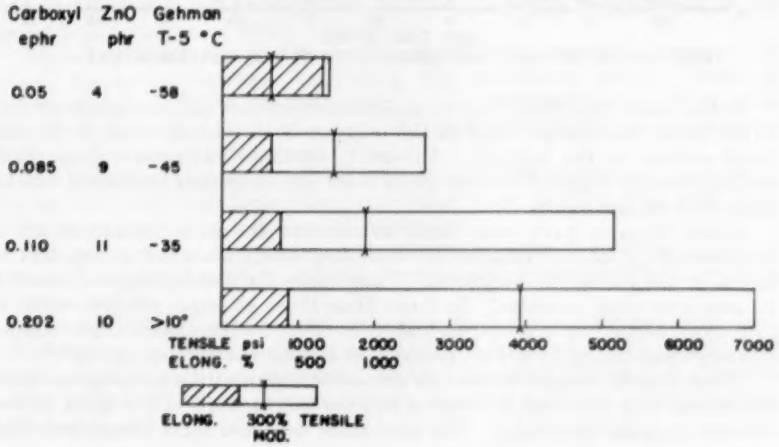


acid copolymer having a carboxyl content of 0.118 equivalent possessed a tensile strength of <100 psi without break at 1600 per cent elongation. After treatment with 0.12 equivalent of sodium hydroxide, as a 2*N* aqueous solution on the

FIG. 6.

INFLUENCE of CARBOXYL LEVEL on METAL OXIDE VULCANIZATES of BUTADIENE – METHACRYLIC ACID COPOLYMERS

(An Indication of the Influence of COOH on Polymer Properties)



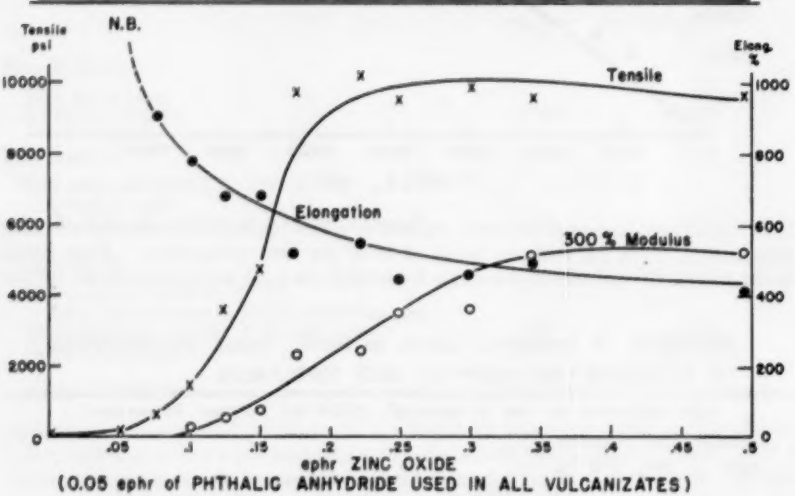
mill followed by molding twenty minutes at 270° F it had a tensile of 1700 psi at an ultimate elongation of 900 per cent. This same polymer[17] with zinc oxide showed 6000 psi tensile strength at an ultimate elongation of 400 per cent (Table III).

With divalent ions such as zinc the chain association is much stronger. Tensile strength increases with increasing carboxyl content (Figures 5 and 6). Copolymers of methacrylic acid with butadiene or with butadiene and acrylonitrile, for example, having carboxyl contents of 0.1 of an equivalent per hundred grams of rubber have shown gum tensiles as high as 11,000 psi with elongations of 400 to 600 per cent. The presence of as little as 0.01 of an equivalent of carboxyl per hundred of rubber is recognizable in metallocarboxylate vulcanizates by the elevation of tensile and modulus values[8].

FIG. 7.

INFLUENCE of ZINC OXIDE LEVEL on a GUM VULCANIZATE of a BUTADIENE / ACRYLONITRILE / METHACRYLIC ACID

55 / 35 / 10 Copolymer of 73% Conversion and 0.099 ephr COOH



(0.05 ephr of PHTHALIC ANHYDRIDE USED IN ALL VULCANIZATES)

It has been established that in metallocarboxylates the maximum amount of the metal chemically bound to the polymer is chemically equal to the carboxyl content of the polymer. However, optimum vulcanizate properties[17] are best insured (Figure 7) by the use of twice the theoretical amount of a metal oxide such as zinc oxide.

Some attempts have been made to improve the poor permanent set of metallocarboxylate vulcanizates by including small amounts of crosslinking agents in the carboxylic polymers. These have the disadvantage of creating gel and increasing modulus. In latex films there is some possible value to such crosslinking but it is not equivalent in effect on permanent set to supplementary crosslinking by sulfur, peroxide or similar vulcanizing agents[19,75].

When a metal compound such as zinc oxide reacts with a carboxylic rubber, zinc atoms may form bonds between two carboxyl groups of the same or two different polymer molecules. The zinc oxide may also form a basic salt with

only one carboxyl group to give a —COOZnOH grouping on the polymer. Either weak bases or weak acids may be used to improve vulcanizate properties by completing the neutralization of the zinc oxide and thereby reducing secondary interlinks[10,14].

Metal oxides as vulcanizing agents for carboxylic rubbers suffer from the disadvantage of being too reactive. Carboxylic rubbers mixed with zinc oxide or other metal oxides cure at room temperature in 48 hours or less. Organic acids, organic acid anhydrides, silica, boric acid, amines and similar reagents were found to be retarders and controllers of the reaction of metal oxides with carboxylic elastomers[17]. It has been found desirable to add the zinc oxide or other metal oxide near the end of the mixing cycle after the incorporation of the controller[14].

Organic acids as controllers materially increase the ultimate tensiles of metal oxide vulcanizates and overcome evidences of precure such as poor flow of stocks in the mold, roughness, and warped or misshapen vulcanizates. Probably the controllers function through one or more of the following types of reactions: (1) devulcanization followed by revulcanization wherein a more uniform distribution of the crosslinks between elastomer chains is achieved, (2) reaction with metal oxide which has been only partially neutralized by polymer carboxyl (–COOZnOH groups) and (3) salt formation with unreacted metal oxide[17].

Basic organic materials may also function as controllers and cure retardants of the metal oxide vulcanization of carboxylic elastomers. No agents more effective than phthalic anhydride, stearic acid, sebacic acid or succinic anhydride have been observed[17].

Finely divided silicon oxides with carboxyl containing elastomers such as carboxylic polyethylacrylate or carboxylic butadiene/acrylonitirle copolymers together with a multivalent metal oxide such as zinc oxide produced relatively less scorchy compounds having good molding properties superior to analogous stocks containing no silicon oxides[13].

Metal oxide gum vulcanizates are self-reinforcing. In the case of a metal oxide vulcanizate with high tensile strength of the carboxylic butadiene/acrylonitrile type terpolymer, stress-strain data for compounds containing EPC black and whiting were essentially the same, both materials functioning as loading agents and not as reinforcing agents and causing a decrease in tensile strength and increase in modulus values[17].

Metallocarboxylate vulcanizates are apparently unusually resistant to ozone, the ozone resistance improving with increasing carboxyl levels in amounts at least up to 0.1 equivalent per hundred of rubber. This ozone resistance probably is dependent upon the poor compression set or stress retention properties of vulcanizates of this type[17,75].

Limitations of zinc oxide vulcanizates of carboxylic elastomers, and especially of carboxylic butadiene copolymers have been poor flex-hysteresis, high compression set and high durometer hardness[17].

The metal salt curing system is applicable to both dry rubber and latex forms of carboxylic rubbers and has found considerable use with carboxylic nitrile rubbers[10].

Carboxylic polyacrylates such as carboxylic polyethylacrylate have been vulcanized by reaction with oxides such as zinc, calcium, cadmium, magnesium, lead, barium, cobalt, tin, strontium, dibutyl tin oxide and similar materials at 150 to 350° F. Such vulcanizates are resistant to ozone, water, sunlight, acids and bases[21].

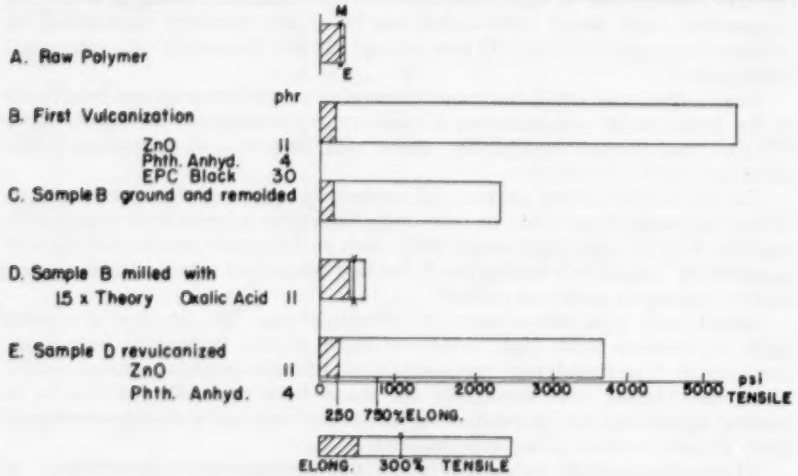
Carboxylic elastomers prepared by the addition of maleic acid anhydride or of ω-mercapto carboxylic acids to synthetic unsaturated elastomers have been vulcanized with metallic oxides or hydroxides such as zinc oxide or calcium oxide[10,17].

Carboxylated scrap natural rubber and butadiene copolymers prepared from vulcanized scrap by the incorporation of maleic anhydride in an extruder-plasticator have been cured with bivalent metallic oxides[42].

Alkaline earth hydroxides in the presence of glycol have been used to give vulcanizates of elastomeric acrylate copolymers of butadiene and of butadiene and acrylonitrile. The ester is hydrolyzed in situ, a metallocarboxylate vulcanizate forming with the resultant carboxyl groups of the elastomer. According to Cooper and Bird[28] who have described the reaction there was no evidence

FIG. 8.

DEVULCANIZATION of a ZINC OXIDE VULCANIZATE of a BUTADIENE / METHACRYLIC ACID 91.4 / 8.6 COPOLYMER of 0.108 ephr CARBOXYL, 78 % CONVERSION



that the glycol formed ester crosslinks by ester interchange. For good vulcanizate properties the presence of 20 to 25 per cent of methyl or ethyl acrylate in the copolymers was found to be desirable. Polymers containing 2-cyanoethyl acrylate were found to cure more rapidly than copolymers of ethyl or methyl acrylate with a glycol and calcium hydroxide system. This *in situ* type vulcanization avoids the scorchiness sometimes encountered in stocks containing free carboxyl groups. This reaction is essentially the same as the vulcanization of polyacrylates by sodium metasilicate, lead oxide and related metal oxides, and salts of weak acids.

Metal oxide vulcanizates of carboxylic rubbers have been devulcanized or reclaimed by treatment with an excess of an organic acid. A cured elastomer was replasticized by grinding to a crumbly mass, adding a carboxylic acid (stearic, oxalic) or an anhydride (phthalic, succinic) and masticating to a smooth sheet[9,17]. See Figure 8.

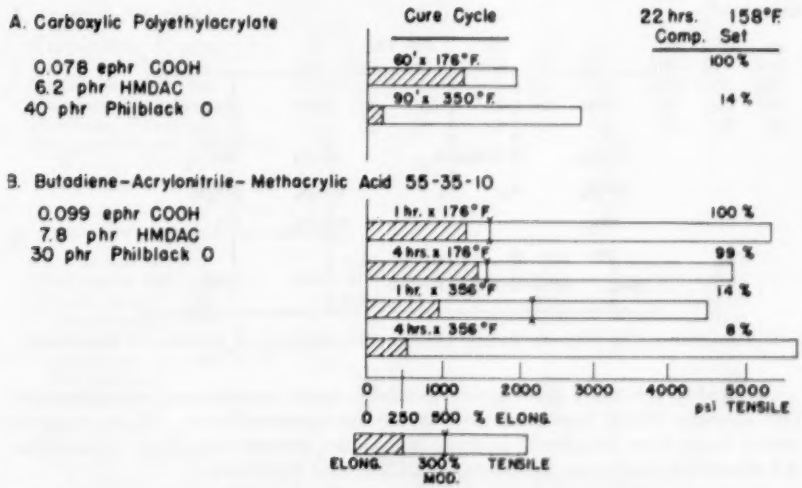
D. DI- OR POLYAMINE VULCANIZATION OF CARBOXYLIC RUBBERS

The vulcanization of carboxylic rubbers with hexamethylene diamine and other polyamines or their carbonates, borates or similar salts has been demonstrated to give useful products[19a].

The vulcanization of polyacrylates and their copolymers by 0.5 to 5 per cent of polymethylene diamines or of polyethylene amines has been reported in the patent literature[44]. No mechanism was offered, but probably hydrolysis of the ester linkage followed by the formation of amide crosslinks occurs. This point of view is substantiated by the fact that carboxylic polyethylacrylate readily react with diamines to give salts and subsequently diamides when subjected to heat[17]. The vulcanization of polyethylacrylate by hexamethylene

FIG. 9.

THE SALT and AMIDE STAGES of VULCANIZATION of CARBOXYLIC ELASTOMERS by HEXAMETHYLENE-DIAMINE CARBONATE



diamine, or the corresponding carbonate with an acidifying agent such as stearic acid to liberate the diamine from the carbonate, depends upon aminolysis of the polyester[17].

Organic diamines have been observed to cause the gelation of acetone-benzene solutions of maleic anhydride cyclized rubber[77]. Thus diamines were indicated as potential crosslinking agents for carboxylic rubbers.

Carboxylic rubbers have been vulcanized with hexamethylene diamine. Preferably the carbonate of hexamethylene diamine was employed as this solid salt was less scorchy and easier to handle than the liquid diamine. Milling at about 120° F sufficiently removed liberated carbon dioxide to avoid porosity in cured stocks. Two stages of cure, probably corresponding to salt formation and diamide formation were indicated by stress-strain and compression-set data (Figure 9). In contrast to the metal oxide vulcanizates, the diamide vulcanizates possessed tensile strengths similar to those of sulfur vulcanizates,

good compression sets, and they required black pigmentation for optimum stress-strain properties[17]. Probable linkages present in hexamethylene diamine vulcanizates[8] are indicated in Figure 10.

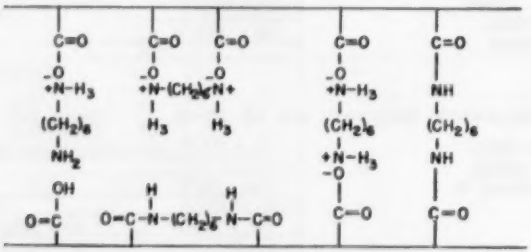
Hexamethylene diamine borate has been used in place of hexamethylene diamine carbonate but offers no advantages[54].

Duomeen T, an amino propyl tallow amine has been used to vulcanize carboxylic rubbers, but is more difficult to incorporate than hexamethylene diamine[19].

Carboxylic polyacrylates have been vulcanized with Trimene Base in recipes similar to those commonly employed with Hycar 4021. Vulcanizate properties comparable to those obtainable with Hycar 4021 have been demonstrated. The reagent was inferior to hexamethylene diamine carbonate giving slower, less firm, vulcanizates with poorer retention of properties at elevated temperatures[19].

Copolymers of alkyl acrylates with acrylic acid (5 to 15 parts) have been cured by heating with polyalkyleen amines such as triethylene tetramine with or without sulfur[45]. Triethylene tetramine is less effective than hexamethylene diamine[19].

FIG. 10.



Linkages Present in Hexamethylene Diamine Vulcanizates of Carboxylic Elastomers

Probably the most satisfactory available agent equivalent to hexamethylene diamine which has been used is 1,8-diaminomenthane. Other reagents which have been employed include biguanide, phenyl biguanide, piperazine, 2,5-dimethylpiperazine, 2,6-diaminopyridine and hydrazine[19].

Some retardation of the hexamethylene diamine salt formation stage has been demonstrated with silica and with whiting[19].

Carboxylic polymers derived from vulcanized scrap natural rubber or butadiene/styrene copolymers by treatment with maleic anhydride have been vulcanized with diamines[42].

Polyacrylates containing up to 0.1 equivalent of anhydride linkages per hundred grams of polymer have been vulcanized by treatment with diamines such as hexamethylene diamine, the vulcanizates possessing the properties of diamine crosslinked polymers[19].

Polyacrylates such as polyethylacrylate and acrylate copolymers such as a butadiene copolymer with 30 per cent of methylacrylate or methylmethacrylate have been vulcanized with hexamethylene diamine. Or a mixture of hexamethylene diamine carbonate and an organic acid such as stearic acid may be used. Vulcanizates having properties analogous to those of hexamethylene diamine vulcanizates of the carboxylic analogs result. Higher levels of hexa-

methylene diamine and more severe curing cycles were required than for carboxylic rubbers, but the vulcanizates are believed to be the same. Vulcanizates of butadiene copolymers had properties essentially the same as those of sulfur vulcanizates of the copolymers[17,19]. The inclusion of ethylene glycol in the vulcanizate appears to aid distribution of the vulcanizing agent and improve the properties of the vulcanizate. (Note the similarity to behavior of metal oxides with acrylate copolymers.) That ethylene glycol in the presence of pyridine failed to vulcanize analogous carboxylic polymers supports the

TABLE IV

EPOXIDE VULCANIZATION OF CARBOXYLIC POLYETHYL ACRYLATE[a]

Recipe									
Polymer	CPEA[b]		100	CPEA[c]		100	Hycar 4021[d]		100
FEF black			40			40			40
Stearic acid			1			1			1
EP 201[e]			1.7			3.5	TETA[f]		1.5
							Altax		2
A. Original Properties									
Cure at 310° F, min	15	30	45	15	30	45	15	30	45
Modulus at 300% psi	120	140	180	160	220	280	220	270	340
Tensile strength, psi	1090	1380	1480	1280	1500	1580	1330	1500	1620
Ultimate elongation, %	1010	700	600	660	500	410	550	470	390
Hardness, Durometer A	50	51	52	52	53	56	58	58	60
Compression set, ASTM-B									
70 hrs at 250° F, %			72			69			
Hardness, Durometer A			46			51			

B. Properties after 24 hours at 300° F			
Cure at 310° F, min	30	30	30
Modulus at 100%, psi	600	1310	380
Tensile strength, psi	1880	1780	1650
Ultimate elongation, %	230	120	280
Hardness, Durometer A	61	65	63
Compression set, ASTM-B			
70 hrs at 300° F	25	22	28
Hardness, Durometer A	58	63	62

[a] From Reference 66.
[b] Carboxylic polyethyl acrylate of 0.012 ephr carboxyl.
[c] Carboxylic polyethyl acrylate of 0.025 ephr carboxyl.
[d] Noncarboxylic Hycar 4021, polyethyl acrylate containing β-chlorethyl vinyl ether.
[e] 3,4-Epoxy-6-methylcyclohexylmethyl-3,4-epoxy-6-methylcyclohexane carboxylate.
[f] Triethylenetetramine.

theory that the ethylene glycol does not participate in the crosslinking reaction. Aging of the vulcanizates before and after curing has been found to improve vulcanizate properties[19].

Just as monovalent metals can enhance the stiffening effect of carboxyl groups on polymer chains and impart a type of apparent vulcanization, so too ammonium salts (such as ammonium carbonate or ammonium borate) and monoamines or their carbonates can stiffen carboxylic rubbers[19].

E. VULCANIZATION OF CARBOXYLIC RUBBERS BY ESTERIFICATION INCLUDING REACTION WITH EPOXIDES AND EPOXY RESINS

Carboxylic rubbers have been crosslinked by esterification with polyhydric alcohols or epoxy compounds[17,55]. Vulcanization of carboxylic butadiene/

acrylonitrile copolymers by the action of the simplest diepoxide, 1,2,3,4-diepoxybutane, has been demonstrated. It is especially useful with carboxylic polyacrylates. Another reactive diepoxide, particularly more suitable as a vulcanizing agent for carboxylic rubbers such as Hycar 1072 is 3,4-epoxy-6-methylcyclohexylmethyl-3,4-epoxy-6-methylcyclohexane carboxylate otherwise known as EP201 (Tables IV and V)[19,66].

TABLE V

A. EPOXIDE VULCANIZATION OF HYCAR 1072[a]

Recipe	
Hycar 1072	100
EPC black	50
EP201	4[b]

Original Properties					
Cure time, minutes	15	30	45	60	60
Cure temperature, ° F	310	310	310	320	350
300% modulus, psi	1420	1800	2380	2860	2830
Tensile strength, psi	2880	3140	3500	3900	3310
Ultimate elongation, %	515	465	400	385	325
Compression set[c], %	88	72	55	40	32
Hardness, Durometer A	65	70	70	70	70
Brittle point, D746-52T, ° C				−55	

B. EPOXIDE VULCANIZATION OF CARBOXYLIC SBR[d]

Recipe	
Carboxylic SBR	100
EPC black	50
EP201[b]	5
MHETPE amine[e]	5

Original Properties					
Cure time, minutes	15	30	45	60	120
Cure temperature, ° F	300	300	300	300	350
300% modulus, psi	1830	2550	2470	2850	3490
Tensile strength, psi	3260	4280	3200	4010	4060
Ultimate elongation, %	500	500	375	400	325
Compression set[c], %	66	63	47	44	35
Hardness, Durometer A	68	70	72	70	70

[a] From Reference 19.
[b] 3,4-Epoxy-6-methylcyclohexylmethyl-3,4-epoxy-6-methylcyclohexane carboxylate.
[c] ASTM test B, 70 hours at 212° F.
[d] Butadiene/styrene/methacrylic acid 71.5/22/6.5, 72% conversion 0.09 equivalent per hundred grams of rubber or carboxyl.
[e] Monohydroxyethyl trihydroxypropyl ethylenediamine.

The epoxy groups of epoxy resins have been used to vulcanize carboxylic butadiene/acrylonitrile copolymers[30,74] prepared both by the reaction of maleic anhydride on butadiene/acrylonitrile copolymers (Hycar 1012) and by direct copolymerization of methacrylic acid with butadiene and acrylonitrile (Hycar 1571). The reaction of epoxy resins such as EPON 1001 is catalyzed by tertiary amines. Epoxy resin-amine adducts were equally effective. Stress-strain properties comparable to those secured with zinc oxide-sulfur cures can be developed with epoxy resins. In an amine-catalyzed carboxylic rubber-epoxide resin system the epoxy group is probably activated by a tertiary amine and then adds to the carboxylic rubber. With severe curing conditions other carboxyl groups may also react with the hydroxyl groups formed. Cure times of 80 minutes at 160° C were effective.

The carboxylic butadiene copolymer Hycar 1072 has been vulcanized by the liquid epoxy resin Araldite 502, by the solid resin Epon 1009, and by similar reagents. Use of a combination cure with metallocarboxylate vulcanization[30] such as may be obtained with zinc oxide results in improved tensile strength and elongation as shown by Table VI.

Carboxylic rubbers from the plastication with maleic anhydride of vulcanized natural rubber or of butadiene/styrene copolymer scrap have been cured by treatment with glycols, or with expoxy resins[42].

TABLE VI

VULCANIZATION OF HYCAR 1072 WITH EPOXY RESINS[a]

A. Recipe

	Hycar 1072			100	Hycar 1072			100
	Araldite 502 resin[b]			40	Epon 1009 resin[c]			80
Original properties	100% modulus, psi	Tensile, psi	Elong., %	Hardness, Durometer A	100% modulus, psi	Tensile, psi	Elong., %	Hardness, Durometer A
10 min at 310° F	150	740	280	53				
20 min at 310° F	275	1100	210	61				
45 min at 310° F	700	1300	150	81	1600	1700	130	96
65 min at 310° F	775	1700	160	84	1725	1820	120	97
100 min at 310° F	1025	1825	140	88				

B. Recipe

	Hycar 1072			100	Hycar 1072			100
	Araldite 502 resin[b]			20	Araldite 502 resin[b]			10
	Stearic acid			1	Stearic acid			1
	Zinc oxide			3.2	Zinc oxide			4.6
Original properties	100% modulus, psi	Tensile, psi	Elong., %	Hardness, Durometer A	100% modulus, psi	Tensile, api	Elong., %	Hardness, Durometer A
10 min at 310° F	225	775	280	56	300	800	340	69
20 min at 310° F	500	1500	230	70	825	2250	260	87
45 min at 310° F	1025	2150	170	90	1400	2575	220	95

[a] From Reference 30.
[b] A liquid epoxy resin.
[c] A solid epoxy resin.

Polyacrylates containing up to 0.1 equivalent of anhydride linkages per hundred grams of polymer (derived from the copolymerization, for example, of ethylacrylate with maleic anhydride in solution) have been vulcanized by treatment with ethylene glycol which would create diester crosslinks[19].

A carboxylic butadiene/acrylonitrile copolymer containing 0.1 equivalent of carboxyl per hundred grams of rubber was successively treated with chemical equivalents of oxalyl chloride and then ethylene glycol to give a crosslinked product believed but not proved to contain ester crosslinks. Vulcanizate properties were inferior to those of a sulfur vulcanizate[19].

F. ANHYDRIDE FORMATION AS A CROSSLINKING REACTION FOR CARBOXYLIC RUBBERS

Uncompounded carboxylic rubbers can be vulcanized by heat alone[17,42]. To bring about the vulcanization of a carboxylic butadiene/acrylonitrile co-

polymer by heat alone requires prolonged treatment at 400° F. Thus, a carboxylic butadiene/acrylonitrile copolymer containing 0.1 equivalent of carboxyl per hundred grams of rubber showed less than 100 psi tensile strength when molded 30 minutes at 300° F but after 2 to 7 hours at 400° F showed a gum tensile strength of 800 psi at 660 per cent ultimate elongation and possessed stress retention properties similar to those of sulfur vulcanizates[8]. Treatment of this polymer with adipoyl chloride in the presence of an acid acceptor reagent gave some vulcanization at room temperature and after 80 minutes at 300° F showed a gum tensile strength of 2200 psi at 445 per cent ultimate elongation[19].

Carboxylic polybutadienes respond to anhydride or thermal vulcanization more readily than their nitrile analogs. A methacrylic acid carboxylic polybutadiene containing 0.11 equivalent of carboxyl per hundred grams of polymer with 40 phr of EPC black, after curing for 120 minutes at 400° F showed 3100 psi micro tensile strength at an ultimate elongation of 485 per cent[19].

Anhydride crosslinks may be established at room temperature in less than two minutes through the use of carbodiimides[19]. The reactions of carbodiimides including anhydride formation from carboxylic acids has been summarized in the literature[59]. Presumably carboxylic rubbers react in a similar manner. The reaction is best demonstrated by treating a solution of a carboxylic rubber such as a carboxylic butadiene/acrylonitrile copolymer or a carboxylic polyethyl acrylate containing 0.01 to 0.1 equivalent of carboxyl per hundred grams of rubber with a chemical equivalent of carbodiimide. Films of carboxylic polymers may be surface cured by this reaction. Upon repeated treatment with solutions of the reagents in solvents which swell the polymers, deep cures may be obtained.

Carboxylic rubbers such as the carboxylic butadiene/acrylonitrile copolymer Hycar 1072 have been vulcanized with carbodiimides, but the stocks were very scorchy and difficult to handle even on small cold mills[19].

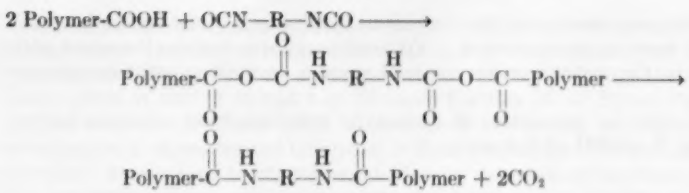
Gelation of solutions of carboxylic rubbers in less than two minutes has been demonstrated with reagents such as N,N′-dicyclohexyl carbodiimide, diisopropyl carbodiimide, and didodecyl carbodiimide. The action of the carbodiimides may be retarded or even inhibited by organic bases[19].

G. DIISOCYANATES AS VULCANIZING AGENTS FOR CARBOXYLIC RUBBERS

It has been reported in the literature[77] that organic compounds having two or more isocyanate groups caused the gelation of acetone-benzene solutions of rubber which had been cyclized with maleic acid anhydride. This indicates that such reagents are crosslinking agents for carboxylic rubbers.

Solutions of carboxylic butadiene/acrylonitrile copolymers or carboxylic polyethyl acrylates in toluene were gelled when treated with p-phenylene diisocyanate. Reaction was much slower than that with the carbodiimides, several hours being required for complete reaction although gradual thickening was observed[19].

Carboxylic butadiene/acrylonitrile copolymers have been crosslinked with diisocyanates such as 1,3-bis(3-isocyanate-p-tolyl) urea, p-phenylene diisocyanate, p-tolyl diisocyanate, and hexamethylene diisocyanate. The reaction is quite scorchy and difficult to handle. Stress-strain properties similar to those obtained with sulfur vulcanizates where no metal oxides were present have been observed[8,20]. Carbon dioxide evolved during the reaction may cause blowing and pitting of vulcanizates. The reaction may be represented as follows:



Vulcanized natural rubber or butadiene/styrene rubber carboxylated by mastication with maleic anhydride has been crosslinked by treatment with diisocyanates[42].

H. VULCANIZATION OF BLENDS OF CARBOXYLIC RUBBERS WITH OTHER RUBBERS

Carboxylic rubbers blend readily with the analogous noncarboxylic rubbers. In vulcanization systems dependent upon the carboxyl group for crosslinking, the noncarboxylic rubber acts as a nonparticipating diluent usually exhibiting more or less of a plasticizing effect[19,42].

Blends of carboxylic butadiene/acrylonitrile copolymers such as Hycar 1072 have been made with noncarboxylic butadiene/acrylonitrile copolymers such as Hycar 1041, 1042, 1043, or 1001. In sulfur vulcanizates, accelerated with zinc oxide and TMTM, the tensile strengths were about equal to an average of those of the component polymers. Each polymer appears to act as a diluent to the unique properties of the other[30].

Blends of Hycar 1072 have been made with natural rubber and with SBR. In the case of sulfur vulcanizates with zinc oxide and benzothiazyl disulfide, properties were essentially an average of those of the two component rubbers[30].

Blends of Hycar 1072 with brominated butyl rubber such as Hycar 2202 showed no improvement in properties over those to be predicted from the properties of the component polymers[30].

Carboxylic rubber hydrocarbons can be used to reinforce polychloroprene compositions in place of the usual reinforcing fillers. Blends of carboxylated vulcanized scrap natural and butadiene/styrene copolymers have been cured with polychloroprene to give practical compounds. The level of carboxyl group incorporation can be used to control the modulus of the vulcanizates[42].

VIII. PROPERTIES OF SELECTED CARBOXYLIC RUBBERS AND THEIR VULCANIZATES

A. CARBOXYLIC POLYBUTADIENE

For applications which require good low temperature and good stress-strain properties without high flexing and low compression set qualities, vulcanizates of carboxylic polybutadienes offer outstanding possibilities[17]. These observations have been verified by other workers[75].

By the selection of optimum conversion, gel content, carboxylic comonomer, and vulcanization conditions, tensiles as high as 11,000 psi at 575 per cent elongation have been obtained for carboxylic polybutadienes. Such polymers possess excellent abrasion resistance[17].

Carboxylic polybutadienes have been prepared with a wide variety of acrylic type carboxylic monomers by emulsion and solvent copolymerization[18]. Copolymers based on methacrylic acid, acrylic acid, sorbic acid, or combinations thereof have been most extensively studied. To obtain uniform carboxyl

content with conversion in the butadiene/methacrylic acid system, methacrylic acid must be proportioned. To obtain uniform carboxyl content with conversion in the butadiene/acrylic acid system, butadiene must be proportioned.

Typical data for properties of carboxylic polybutadiene vulcanizates are presented in Table III of Reference 17.

B. CARBOXYLIC COPOLYMERS OF BUTADIENE AND ACRYLONITRILE

Carboxylic copolymers of butadiene and acrylonitrile have been prepared in emulsion with a number of acrylic acid type comonomers. Specially considered have been acrylic acid, methacrylic acid, sorbic acid, cinnamic acid, itaconic acid, crotonic acid, monomethyl itaconate, and fumaric acid[18,75].

The most extensively studied carboxylic terpolymer systems of butadiene and acrylonitrile have been those in which methacrylic acid was the carboxylic comonomer. Nitrile contents from zero to 50 per cent and carboxyl contents from zero to 25 per cent have been studied[17,19]. Acrylonitrile tends to improve the uniformity of carboxyl content with conversion. In the butadiene/acrylonitrile 55/45 and 67/33 systems the replacement of acrylonitrile by 0.1 equivalent or less of methacrylic acid gave terpolymers having fairly uniform carboxyl distribution. The lower the acrylonitrile content the less uniform the distribution[17]. Or, it may be said that the more methacrylic acid employed the more acrylonitrile required to insure uniform carboxyl distribution[75].

The replacement of acrylonitrile by a chemical equivalent of methacrylic acid had virtually no effect on the oil resistance of the polymers. Thus the carboxyl group possesses oil resistance similar to that of the nitrile group[17].

A commercially available carboxylic butadiene copolymer is Hycar 1072. Hycar 1072 mills readily and is actually somewhat more plastic when warm than the analogous noncarboxylic polymer Hycar 1042. Similar scorch times have been observed for Hycar 1072 and Hycar 1042 in tetramethyl thiuram disulfide (TMTD)—zinc oxide-sulfur vulcanization systems. Hycar 1072 was somewhat scorchier in a tetramethyl thiuram monosulfide (TMTM)—zinc oxide accelerated sulfur system. Scorch tendencies, especially during bin aging may be reduced by the inclusion of stearic acid. Conventional recipes for the vulcanization of butadiene/acrylonitrile copolymers need little or no modification for satisfactory cures with analogous carboxylic polymers[65].

Very high gum tensiles of the order of 5500 psi at elongations in excess of 400 per cent have been reported for Hycar 1072 and related polymers[17,49,65]. In black-sulfur-zinc oxide recipes, superior stress-strain properties at elevated temperatures (e.g., 250° F), high compression sets, phenomenal abrasion resistance, and better low temperature brittleness properties were observed for Hycar 1072 compared with the noncarboxylic analog Hycar 1042. The vulcanizates of Hycar 1072 show only stiffening at temperatures at which similar vulcanizates of the noncarboxylic analog Hycar 1042 have become brittle, hence they are useful at lower temperatures in many applications[49]. (Table II, Table V, Table VII, Table VIII.)

In identical black recipes based on TMTD and zinc oxide, Hycar 1072 as compared with Hycar 1042 showed higher tensiles, lower elongation, higher modulus and hardness, higher tear strength, and higher compression set. Resistance to oils, fuels, solvents and hot air were similar but Hycar 1072 in contrast to Hycar 1042 tended to retain its hardness or increase in hardness in hot oils[17,19,49,65].

A comparison of Hycar 1072 and Hycar 1042 in equivalent curing systems at equivalent hardness as regards De Mattia flex crack resistance[50] has shown that whereas Hycar 1072 at room temperature had 0.2 to 0.5 the flex life of Hycar 1042, at 250° F it had 5 to 10 times the flex life of Hycar 1042.

The response of Hycar 1072 to combined sulfur and metallocarboxylate cures has been characterized in several recipes employing different acceleration systems. Stocks tend to show a rapid Mooney scorch-time decrease during the first two weeks of aging. Stearic acid retarded the scorch tendencies[49].

Because of the superior gum tensile properties of Hycar 1072 compared with its noncarboxylic analogs in sulfur recipes containing zinc oxide it is better suited for loading with nonblack pigments. This has been demonstrated with atomite, barytes, talc, and similar pigments[49].

TABLE VII

COMPARISON OF METALLOCARBOXYLATE AND A COMBINED METALLOCARBOXYLATE AND SULFUR VULCANIZATE OF HYCAR 1072 WITH A HYCAR 1042 VULCANIZATE[a]

Recipe	*A*			*B*			*C*		
	Hycar 1072		100	Hycar 1072		100	Hycar 1042		100
	Stearic acid		1	Stearic acid		1	Stearic acid		1
	Zinc oxide		9.3	Zinc oxide		5	Zinc oxide		5
				TMTD		3	TMTD		3
				FEF black		40	FEF black		40
				Sulfur		0.5	Sulfur		0.5
Original Properties									
Cure time, minutes	15	30	45	15	30	45	15	30	45
Cure temperature, ° F	310	310	310	310	310	310	310	310	310
100% modulus, psi	280	290	320	1620	1350	1870	520	490	550
Tensile strength, psi	5100	5750	4420	3870	3680	3880	2670	2640	2880
Ultimate elongation, %	520	560	490	300	280	250	300	270	300
Hardness, Durometer A	72	73	73	84	83	85	71	70	72
Compression set, ASTM-B[b]			95			20			11
Hardness, Durometer A			70			83			70
Tear resistance, lb/in.			210			270			200
Properties Measured at 250° F									
Tensile strength, psi			190			2260			840
Ultimate elongation, %			1000+			290			160
Tear resistance, lb/in.			40			120			80

[a] Data from Reference 49. Hycar 1042 is the noncarboxylic analog of Hycar 1072.
[b] 70 hours at 212° F.

Hycar 1072 and other carboxylic copolymers of butadiene with acrylonitrile in vulcanizates containing zinc oxide or other metal oxide possess apparently better ozone resistance than the noncarboxylic analog probably due to their poor stress retention[17]. The ozone resistance increases with increasing carboxyl level[19,75].

The hardness of Hycar 1072 is greater than that of Hycar 1042 when polyvalent metal ions are present. The hardness of a Hycar 1072 vulcanizate decreased more rapidly as the operating temperature was raised than did a similar vulcanizate of Hycar 1042. In the TMTD-zinc oxide recipe the hardness is of the order of 80 Shore A compared with 65 for Hycar 1042. This hardness may be reduced by the inclusion of softeners or by reducing the amount of reinforcing pigment. Use of either of these methods to reduce hardness causes loss of tensile, and at equal hardness achieved by these methods properties of Hycar 1072 and Hycar 1042 approach each other. In a zinc oxide-

TMTD recipe 10 phr of FEF black with Hycar 1072 gave essentially the same hardness as 40 phr with Hycar 1042. At equal hardness, Hycar 1072 possesses much better abrasion resistance[49,65] than Hycar 1042.

In general, the higher the black loading in combination sulfur-zinc oxide vulcanizates of Hycar 1072 the higher are the hardness and modulus, the lower is the elongation, the poorer is the low temperature flexibility, and the poorer is the compression set[49].

TABLE VIII

COMPARISON OF THREE CURING SYSTEMS FOR HYCAR 1072[a]

Recipe	*A*		*B*		*C*	
	Hycar 1072	100	Hycar 1072	100	Hycar 1072	100
	Stearic acid	1	Stearic acid	1	Stearic acid	1
	Sulfur	1.5	Sulfur	1.5	FEF black	40
	FEF black	40	FEF black	40	Zinc oxide	10
	TMTM	0.4	TMTD	2		
	Zinc oxide	5	CHBS	0.75		
			Zinc oxide	5		
Mooney Scorch at 250° F—small rotor (cure time Δ30, minutes)						
Original	>30		16¼		21¼	
Shelf aged 6 weeks	16¼		12¾		13¼	
Original Properties						
Cure at 310° F, minutes	15	30	45	15	30	45	15	30	45
100% modulus, psi	1190	1130	1100	1760	1720	1850	1380	1550	1430
Tensile strength, psi	3600	3280	3450	3670	3920	4000	4130	4100	3900
Ultimate elongation, %	300	280	280	200	200	210	330	340	320
Hardness, Durometer A	86	86	85	87	87	87	88	88	88
Compression set[b]									
22 hours at 158° F			46			17			100
70 hours at 212° F			60			27			100
Hardness, Durometer A			83			84			86
Tear resistance[c], lb/in.			220			170			320
Properties at 212° F									
100% modulus, psi			530			870			170
Tensile strength, psi			2200			2290			420
Ultimate elongation, %			300			200			950
Tear resistance[c], lb/in.			150			90			150

[a] Data from reference 49.
[b] ASTM Method B. Block cured 45 minutes at 310° F.
[c] Die C. Tear with the grain.

In studies based on Hycar 1072 with combination sulfur-metallocarboxylate cure, Harflex 300X at 22 phr gave the best tensile strength, modulus, and room temperature tear resistance. The best hot properties, lowest hardness, and highest elongation[49] were obtained with 25 phr of Santicizer 300.

In zinc oxide gum vulcanizates tensile strengths[17,19] up to 11,000 psi (micro) at elongations of 400 to 550 per cent have been observed for butadiene/acrylonitrile/methacrylic acid charged 55/36.4/8.6, 55/35/10, and 67/36.4/8.6. For 70/20/10 and 60/30/10 systems values of 5000 to 7650 psi (macro) at elongations of 425 to 450 per cent have been reported[75].

The use of calcium hydroxide or a combination of calcium hydroxide with zinc oxide has been reported to give metallocarboxylate vulcanizates having

lower moduli, greater elongation and better tensile and tear properties with a butadiene/acrylonitrile/methacrylic acid 57/40/3 terpolymer than could be achieved with zinc oxide alone[75].

Dutrex 20 has been reported to be the best of a series of external plasticizers for metallocarboxylate vulcanizates of butadiene with acrylonitrile and methacrylic acid terpolymers[75].

Tetrapolymers of butadiene, acrylonitrile and methacrylic acid have been prepared with various acrylates in a range of monomer proportions. Plasticizing action has been noted with ethyl acrylate, butyl acrylate and lauryl methacrylate[17,19,75]. Either this internal plasticization or the use of external plasticizers caused reduction of modulus and tensile[30].

The possibility that acrylic type acids having the carboxyl group remote from the polymer backbone might give a polymer containing longer crosslinks and hence possessing lower modulus values and related properties has been considered. Such a copolymer of butadiene and acrylonitrile might give an oil resistant polymer of improved low temperature properties[19,75].

Sorbic acid gave terpolymers whose films reportedly showed improved tear strength without increased modulus values. Terpolymers in which methacrylic acid in the system butadiene/acrylonitrile/methacrylic acid 57/40/3 was replaced by methacryloxy propionic acid or by α-[α-(α-methacryloxy propionoxy)propionoxy] propionic acid have been described. There is evidence, in the opinion of V. A. Miller and others, that some flexibility has been imparted to the metallocarboxylate vulcanizates of the polymer[75]. A disadvantage in these two monomers as well as with acryloxypropionic acid[19] is that although the carboxyl group involved in metallo carboxylate salt formation is removed to a greater distance from the polymer chain the stiffening effect of a carbonyl group is still as proximate to the polymer chain as in methacrylic acid.

C. CARBOXYLIC COPOLYMERS OF BUTADIENE AND STYRENE

The substitution of a carboxylic acid such as methacrylic acid for styrene in butadiene/styrene copolymers resulted in increased tensiles and moduli, lowered elongations, increased hardness, poorer flex and hysteresis properties, and elevated Gehman low temperature properties in typical sulfur vulcanizates. Without added reinforcing pigments, zinc oxide gum cures gave stress-strain properties equalling or surpassing the properties of the analogous butadiene/styrene copolymers of the same butadiene content in black reinforced sulfur vulcanizates[17].

Styrene does not improve the distribution of methacrylic acid in copolymerization with butadiene, the methacrylic acid entering the copolymer at greater than the charged level. Uniformity of carboxyl content can be achieved by proportioning the methacrylic acid or using selected mixtures of methacrylic with acrylic acid[17,75].

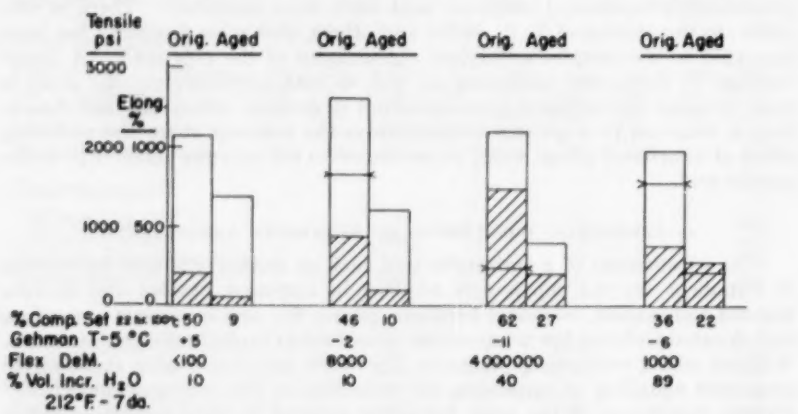
The preparation of carboxylic butadiene/styrene copolymers wherein the carboxyl group was remote from the polymer backbone rather than proximate to it has been considered with the hope of producing metallocarboxylate vulcanizates containing longer crosslinks and hence possessing lower modulus values and related properties[75]. Copolymers with β-acryloxypropionic acid and related materials in which polar groups were still proximate to the chain although the crosslink was longer have not been effective[19,75]. β-Methacryloxypropionic acid, and 12-acryloxystearic acid have been copolymerized[19].

D. CARBOXYLIC COPOLYMERS OF POLYACRYLATES

Ethyl acrylate rubbery copolymers with methacrylic and acrylic acid vulcanized with zinc oxide showed gum tensiles up to three times those of the best black vulcanizates obtained with customary cures of polyethyl acrylate, Hycar 4001 (discontinued) or Hycard 4021 depending on carboxyl content, but showed inferior compression sets and related properties. Carbon black did not act as a reinforcing agent for the zinc oxide vulcanizates but was a filler. With increasing carboxyl content, tensile rose, elongation dropped, and Gehman values increased. In the vulcanization recipes commonly employed with Hycar 4021, increasing carboxyl levels resulted in increased hardness, increased 300 per cent moduli, reduced elongation, improved compression set, and elevated Gehman T-5 values[17].

FIG. 11.

HEXAMETHYLENE DIAMINE CARBONATE VULCANIZATES of CARBOXYLIC POLYETHYLACRYLATES


Carboxyl ephr 0.047 0.022 0.012 Hycar 4021
HMDAC phr 3.8 1.8 1 Trimene Base 3
Philblack O phr 40 40 40 40
Tensile psi
Orig. Aged Orig. Aged Orig. Aged Orig. Aged
3000
Elong. %
2000 1000
1000 500
0 0
% Comp. Set 22 hr. 302°F 50 9 46 10 62 27 36 22
Gehman T-5 °C +5 -2 -11 -6
Flex DeM. <100 8000 4000000 1000
% Vol. Incr. H2O 10 10 40 89
212°F - 7 da.

Many carboxylic acrylates have been made including copolymers of methyl, ethyl, propyl, *n*-butyl, isobutyl, tert-butyl, 2-ethylhexyl, decyl, dodecyl, tridecyl, tetradecyl and octadecyl acrylates (and some methacrylates) with such comonomers as acrylonitrile, divinyl benzene, and polyallyl ethers[19,21].

The phenomenon termed negative thixotropy by A. Katchalsky and others[58] has frequently been observed with alkali neutralized carboxylic polyethyl acrylates in ethanol and in pyridine solutions. Such solutions have shown a several hundred fold increase in consistency when stirred or shaken changing from limpid liquids to jellied masses[20].

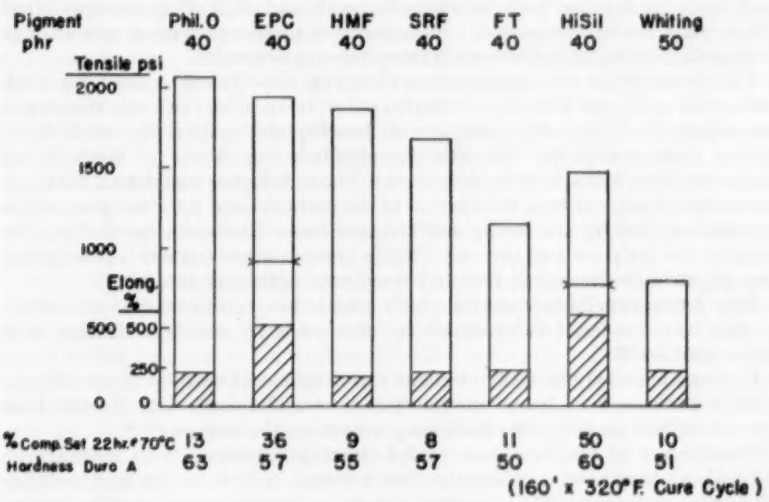
Several copolymers of acrylates and copolymerizable anhydrides have been prepared in solvents such as benzene, toluene, methyl ethyl ketone and acetone. Thus, ethyl acrylate has been copolymerized with up to 15 per cent of maleic anhydride[19,54].

Hexamethylene diamine, its aqueous solution, or preferably its carbonate

has been used to vulcanize carboxylic polyacrylates. Salt formation occurred at or near room temperature. Diamide formation occurred at elevated temperatures. A carboxylic polyethyl acrylate containing 0.5 per cent each of methacrylic and acrylic acid when vulcanized with one part of hexamethylene diamine carbonate per hundred of polymer gave diamide cures which when compared at equal pigment loading with a Trimene Base vulcanizate of Hycar 4021 (polyethyl acrylate) showed comparable stress-strain properties and hardness, retention of stress-strain properties at elevated temperatures, and similar reinforcement by blacks, whiting, and Hi Sil. Equal or better De Mattia flex life, and compression set have been observed as well as similar excellent

FIG. 12.

PIGMENTATION of HEXAMETHYLENE DIAMINE CARBONATE VULCANIZATE of CARBOXYLIC POLYETHYLACRYLATE (0.022 ephr)



ozone resistance, comparable Gehman values, comparable swell in ethyl alcohol, hexane and benzene at room temperatures; similar swell in ASTM No. 1 and No. 3 at 212° F; and superior resistance to boiling water[17]. (Figures 11, 12).

Much lower levels of carboxyl are required for optimum vulcanizate properties of carboxylic polyethyl acrylates with hexamethylene diamine, diepoxides or metal oxides than with carboxylic butadiene/acrylonitrile copolymers. Carboxyl levels of 0.01 to 0.02 equivalent per hundred grams of rubber appear to be optimum while 0.05 to 0.1 equivalent per hundred grams of rubber are preferred for the carboxylic butadiene/acrylonitrile copolymers[19].

E. MISCELLANEOUS CARBOXYLIC RUBBERS

The preparation of copolymers of butadiene, trifluoroacyrlonitrile and methacrylic acid has been reported[75].

Copolymers of butadiene and methacrylic acid and either acrylamide or methacrylamide have been prepared. Latex containing as much as five parts

acrylamide in the presence of three parts of methacrylic acid tends to thicken or gel. The acrylamide appeared to have some plasticizing action thereby improving the tear of zinc oxide vulcanizates. Terpolymers with acrylonitrile present showed similar behavior[75].

N-Phenylmaleamic acid did not copolymerize with butadiene alone but did copolymerize when acrylonitrile was also present. A butadiene/acrylonitrile/N-phenylmaleamic acid terpolymer initially charged 54/40/6 has been described. Cast films of the polymer were snappy. Very little cure was achieved with zinc oxide. Maleamic acid itself had little or no tendency to copolymerize[75].

Benzoylacrylic acid has been copolymerized with butadiene and acrylonitrile. Acrylonitrile tends to give uniformity of carboxyl content with conversion. Benzoylacrylic acid has also been copolymerized with butadiene and methyl methacrylate[75].

The preparation in an acidic cationic system of butatiene/acrylonitrile copolymers containing both methacrylic acid and N,N-diethylamino ethyl methacrylate has been reported. Superiority of these copolymers over analogous 2-methyl-5-vinylpyridine copolymers was not evident[75].

The preparation of butadiene/acrylonitrile copolymers containing both methacrylic acid and 2-methyl-5-vinylpyridine in an acidic cationic recipe has been reported. The polymerization of 2-methyl-5-vinylpyridine or 2-vinylpyridine onto carboxylic butadiene/acrylonitrile copolymer in latex in an alkaline medium has also been described. The conclusion was drawn that any reinforcement derived from interaction of the carboxyl and pyridine groups was far overshadowed by the strong salt linkages formed between the carbyoxylic groups of the polymer and the metal oxide in metallocarboxylate vulcanizates. Some slight improvement in tear and tensile strength may result[75].

Poly-2-neopentylbutadiene-1,3 which does not respond to sulfur vulcanization has been rendered vulcanizable by zinc oxide by copolymerization with methacrylic acid[19].

Carboxylic terpolymers of butadiene and acrylic acid with up to ten percent of ethyl methacrylate, lauryl methacrylate, or isooctyl acrylate showed that these esters had an internal plasticizing action on the polymer[18,19].

Copolymers of isoprene and of 2,3-dimethylbutadiene with methacrylic acid with and without acrylonitrile also present, in both sulfur and metallocarboxylate vulcanizates behave similarly to analogous butadiene copolymers, but have inferior low temperature properties[19].

A number of polymers related to the tetrapolymer system butadiene/ethyl acrylate/methyl methacrylate/methacrylic acid system have been prepared and have shown typical properties of carboxylic rubbers. Butadiene contents varied from 55 to 85 per cent. Isoprene has been used in place of butadiene. Ethyl methacrylate has been used in place of methyl methacrylate. Methyl acrylate has been used in place of ethyl acrylate[86].

Copolymers of chloroprene with methacrylic and acrylic acids have been prepared having a range of carboxyl levels, but predominantly less than 0.1 equivalent of carboxyl per hundred grams of polymer. They show typical carboxylic rubber vulcanization reactions[17,19].

IX. ADHESIVE PROPERTIES OF CARBOXYLIC RUBBERS

Butadiene/methacrylic acid copolymers have been employed for the adhesion of rubber to steel. For maximum adhesion, the copolymer should pos-

sess sufficient diene content for vulcanization to a rubber and sufficient carboxyl groups to secure high adhesion to steel. The optimum acid content appears to be 15 to 24 per cent[41]. Bonding of both natural and synthetic rubbers to metal by a single coat of adhesive has been reported. Solutions (2 to 10 per cent) of butadiene/methacrylic acid copolymers in cyclohexanone or dioxane containing a peroxidic accelerator were employed[39].

Cements prepared from the carboxylic copolymer of butadiene and acrylonitrile, Hycar 1072, together with phenolic resins have shown good adhesion to metals[49,65].

Zinc oxide or other metal oxides or salts may be compounded with carboxylic rubbers such as Hycar 1072 in suitable solvent such as methyl ethyl ketone. The shelf life of such a cement may be much improved by the inclusion of a few parts of ammonia or amines which can be volatilized when the cement is employed[66].

A 30 per cent cement in methyl ethyl ketone of a carboxylic butadiene/acrylonitrile copolymer containing zinc oxide (10 phr) and stearic acid (5 phr) has given a bond between aluminum foil and Kraft paper which was stronger than the paper. The cement has also been used as an adhesive for nylon to plastisol constructions[49]. Good bonds between Nylon and rubber have been observed[30].

Maleic anhydride rubbers have been reported to be adhesive agents for artificial silk[57]. They have also been considered in metal adhesions[53].

A butadiene/acrylonitrile copolymer modified with maleic anhydride has been recommended as a component of an adhesive composition for bonding polyperfluorovinyl chloride to metal. The adhesive composition also contained polychloroprene and a rosin acid[38].

Carboxylic polyacrylates have been found to be excellent laminating adhesives for adhering many synthetic film surfaces to each other and to metal foils, for the adhesion of glass to itself and other surfaces, for the adhesion of wood to itself and other surfaces, and for the lamination of metal films. They may be applied from solvent or from aqueous dispersions. Curing agents such as metal oxides, metal salts, epoxy resins, polyamines, and pigment additives may be used to adapt the materials to a variety of applications[1,20,43].

Aqueous solutions of copolymers of conjugated dienes with acrylic or methacrylic acid have been described as bonding agents for rubber to fabric laminations. Use of a dispersion of a butadiene/acrylic acid copolymer (charged 30 per cent by weight) in aqueous potassium hydroxide as a dip for rayon tire cord has been described[62].

X. BLENDS OF CARBOXYLIC RUBBERS WITH NON-ELASTOMERIC POLYMERS

Blends of the carboxylic butadiene/acrylonitrile copolymer, Hycar 1072, with polyvinyl chloride were more easily prepared than those with the analogous noncarboxylic Hycar 1042. The blends extruded more smoothly, possessed much improvement in respect to low temperature brittleness, improved abrasion resistance and greater thermoplasticity[55].

In comparable uncured blends with the polyvinyl chloride Geon 101EP, Hycar 1072 exhibits higher tensile, higher modulus, less low temperature brittleness, and lower elongation[49] than Hycar 1042. Blends have been prepared both on the mill and in latex.

The carboxylic butadiene/acrylonitrile copolymer, Hycar 1072, as com-

pared with its noncarboxylic analog, Hycar 1042, has been found superior when employed in phenolic molding resins for the improvement of impact strength and other purposes. Hycar 1072 possessed greater compatability and imparted greater tensile strength[49,65] when employed with such resins as Durez 12687 and G.E. 12316.

XI. MISCELLANEOUS APPLICATIONS OF CARBOXYLIC RUBBERS

In view of the several adhesive applications of carboxylic rubbers it is interesting to note that a 70/25/5 terpolymer of butadiene, acrylonitrile, and sorbic acid has been reported to be a lap-resistant polymer, that is to have less tendency to cling to textile filaments than the analogous noncarboxylic polymer[22].

The carboxylic butadiene/acrylonitrile copolymer, Hycar 1072, in a shoe sole formulation has shown superior resistance to abrasion and tear, good tensile strength, rebound and flexure performance[49]. These properties combined with the oil resistant properties of the nitrile rubbers commend Hycar 1072 for oil resistant shoe sole applications.

XII. LATEX APPLICATIONS OF CARBOXYLIC RUBBERS

Carboxylic rubbers have film forming properties superior to those of analogous noncarboxylic polymers. Because of the reactivity of the carboxyl groups with themselves and with metal ions, wet films of excellent strength have been obtained from both uncompounded and compounded latex. Thus, it is possible to prepare rubber articles by dipping a form, such as that for a glove, coated with a suitable solution containing poylvalent ions, such as calcium, zinc or magnesium, into carboxylic latex. A strong rubber film which may be further strengthened by hot air curing is thus obtained. Also such agents as zinc oxide or sodium aluminate may be dispersed in the latex. Sodium aluminate has the unique advantage of being a water soluble vulcanizing agent. Where oil resistance is an advantage dipped goods or cast films may be prepared from carboxylic butadiene/acrylonitrile copolymers. Rubber gloves, diaphragms, coatings and linings which may come in contact with solvents, petroleum oils, fats or similar materials may be fabricated in this manner[14,48].

Rubber articles have been prepared by coagulant dipping from carboxylic polybutadiene, carboxylic butadiene copolymers with acrylonitrile, carboxylic butadiene copolymers with styrene, carboxylic polyethyl acrylates, and carboxylic polychloroprenes. Such articles as gloves, pen sacs, bottle liners, tubing, diaphragms, and small containers have been prepared. Excellent dipped goods have been prepared without compounding curative agents into the latex. In this case requisite polyvalent ions (e.g., Ca^{++}) were derived from the coagulant dip solutions employed. Gloves of excellent oil resistant properties have been prepared from carboxylic butadiene/acrylonitrile copolymers. These metallocarboxylate vulcanized articles are not sensitive to aqueous alkaline or acid hydrolysis[55].

Latexes of carboxylic butadiene/styrene copolymers have given cured films with zinc oxide possessing excellent tensile strength and related properties[21,55].

In general, a lower carboxyl content is required in dipped films to obtain a given tensile strength in metallocarboxylate vulcanizates than is required for milled stocks.

Blends of carboxylic copolymers of butadiene and acrylonitrile with borated casein have provided excellent adhesion of vinyl sheeting and vinyl plastisol coatings to paper, nylon and rayon[43].

The carboxyl group improves the penetrating power of a given copolymer system for paper, cotton fibers, and fabrics. The carboxylic butadiene/acrylonitrile copolymer latexes have been used as pigment binders for leather, the saturation of paper and paper boards, the impregnation of cork, the modification of water soluble phenolic resins for paper treatment, and the adhesion of vinyl plastisol coatings to rayon and nylon fabrics[14,48]. Leather products may be upgraded by impregnation with carboxylic latexes, especially carboxylic butadiene/acrylonitrile copolymers. Abrasion, chemical resistance, flexibility, aging and impermeability to liquids and gases is improved by such treatment[48].

Advantage may be taken of the improved fabric penetration imparted to latex by the inclusion of carboxyl groups for the enhancement of rubber to fabric adhesions. Maximum adhesion is achieved when carboxylic groups are included in both the impregnating latex and the rubber polymer to be adhered thereby permitting inter-crosslinks[43].

The inclusion of acrylonitrile in carboxylic ethyl acrylate or carboxylic polybutyl acrylate polymer imparts increased oil resistance and poorer low temperature properties in proportion to the amount of acrylonitrile introduced[20,55].

Carboxylic acrylate latexes have been used for saturating paper, the products exhibiting good light and heat aging properties and fold resistance[31].

Polyacrylates of alcohols having one to four carbon atoms and copolymerized with 4 to 7 per cent of acrylic or methacrylic acid have been described as pigment binders for preparing coated paper products. The alkali metal salts of the carboxylic copolymers were employed. Salts of similar carboxylic polyacrylates in which the carboxyl groups were derived from itaconic acid, aconitic acid, maleic acid, fumaric acid, or the dimer or trimer of methacrylic acid have also been described for this application[68,69].

There is some evidence that sorbic acid in place of methacrylic acid in carboxylic butadiene/acrylonitrile copolymers imparts improved tear resistance to dipped films[55,75].

XIII. LIQUID CARBOXYLIC COPOLYMERS

Liquid carboxylic copolymers of most of the common elastomer systems have been prepared. Carboxylic polybutadienes, butadiene/styrene, and butadiene/acrylonitrile copolymers have been extensively studied and products ranging in molecular weight from 700 to molecular weights giving soft, nearly solid rubbers have been made[20] (Table IX). These polymers have been vulcanized by sulfur, metallocarboxylate, epoxide, diamine, and anhydride corsslinks. The lower the molecular weight the more facticelike rather than rubberlike were the vulcanizates[20,43].

Liquid carboxylic copolymers have been prepared in emulsion systems using high levels of modifier agents such as mercaptans or bis xanthogens to control molecular weight. They have also been prepared in solvents which function as chain terminating agents (e.g., triisopropylbenzene, cumene, bromotrichloromethane, methyl chloroform, methyl ethyl ketone, etc.)[20].

Cooper[27] has reported the preparation of metallic salts of liquid copolymers of butadiene with acrylic or methacrylic acids. A butadiene copolymer with 12.6 per cent methacrylic acid having a molecular weight of the order of 7000

was described. Zinc salts were characterized as "soluble thermoplastic substances with similar rheological properties to the silicone 'bouncing putty.'" Satisfactory polymers for this purpose contained 4 to 10 per cent of combined acid. Larger amounts of acid gave hard products with little tendency to flow. Lead and calcium salts were harder at room temperature than the zinc salts. The polymers had viscosities of 0.07 to 0.21 in benzene. Evidence was advanced which suggested that the salts prepared with zinc were basic zinc salts and thus may be represented by a formula Polymer-(COOZnOH)n.

Liquid carboxylic polybutadienes of molecular weights as low as 910 containing an average of one carboxyl per molecule have been prepared. Such polymers do not solidify with carboxylic crosslinking agents. With higher

TABLE IX

LIQUID CARBOXYLIC COPOLYMERS[a]

Polymer type	Monomer ratio	Conv., %	Carboxyl, ephr[b]	Mol. wt.[c] (cryoscopic)	Viscosity[d] (Brookfield)
B/MA	96/3	58	0.04	910	210
B/MA	95/5	60	0.068	1100	600
B/MA	90/10	60	0.13	1080	1950
B/MA	89/11	93	0.11	2000	40,000
B/S/MA	85.5/4.5/10	21	0.166	680	2000
B/S/MA	85.5/4.5/10	41	0.156	950	2200
B/S/MA	85.5/4.5/10	53	0.140	1340	4900
B/S/MA	85.5/4.5/10	76	0.122	1630	8800
B/V/MA	67/24.4/8.6	90	0.094	2064	44,300
B/V/MA	55/42.14/2.86	90	0.027	2140	68,600
B/V/MA	55/42.14/2.86	91	0.030	[g]	>100,000[e]
B/V/MA	55/42.14/2.86	82	0.032	[g]	ML-4'-RT-21[f]
B/V/MA	55/42.14/2.86	90	0.030	[g]	ML-4'-RT-51[f]
B/V/MA	55/25/20	89	0.190	1360	40,000
B/V/MA	55/25/20	80	0.192	1420	>100,000[e]
B/V/MA	55/25/20	89	0.190	1700	>100,000[e]

B = Butadiene, MA = Methacrylic acid, S = Styrene, V = Acrylonitrile.

[a] Data from Reference 20. Prepared with tertiary mercaptan modification.
[b] Analytically determined equivalents per hundred grams of polymer.
[c] Sulfur analyses indicate essentially one thioalkyl (—SR) radical per molecule thus contributing about 200 units of molecular weight per molecule.
[d] Brookfield Viscosity at 50° C expressed in centipoises.
[e] Could be measured at higher temperatures.
[f] Room temperature Mooney viscosity, large rotor. A soft near-solid copolymer.
[g] Too high to measure cryoscopically.

carboxyl levels and/or molecular weights solidification readily was achieved. Similar carboxylic liquid 3 per cent styrene copolymers with butadiene having molecular weights as low as 680 have been prepared[20].

Liquid carboxylic butadiene/acrylonitrile copolymers have been converted into cured films by treatment with epoxy resins or mixtures of epoxy resins with polyamides[20]. They have also been solidified with diepoxy butane, with 3,4-epoxy-6-methyl-cyclohexylmethyl-3,4-epoxy-6-methylcyclohexane carboxylate, with zinc oxide and other metal oxides. Such crosslinked liquid polymers have been found useful as pigment binders. As much as eight times their weight of clays, carbon blacks and other materials have been bound into solid masses which may be used for flooring, linoleum, and similar applications.[20]

Leather, paper, fabrics and other porous materials have been impregnated with liquid carboxylic copolymers which were then cured in these materials

by treatment with crosslinking agents. Aluminum isopropylate, N,N-dicyclohexyl carbodiimide and similar agents have been employed in solvents for this purpose. Aqueous solutions of sodium aluminate and similar salts may also be employed[19].

Liquid carboxylic butadiene/acrylonitrile copolymers have been found to be more efficient softeners for carboxylic Hycar 1072 than are analogous non-carboxylic liquid polymers[20].

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RUBBERS FROM BASIC MONOMERS. VINYLPYRIDINE POLYMERS

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INTRODUCTION

Interest in vinylpyridine and vinylpyridine derivatives as monomers for production of synthetic rubber was evidenced immediately prior to World War II. In 1939 and 1940, European patents were issued on polymerization of vinylpyridines and their copolymerization with other monomers. Research in the United States on vinylpyridines and their derivatives as comonomers began in the early 1940's. Much of the early work was conducted under the Government synthetic rubber program with work carried out by several of the participating universities and rubber companies. At that time, vinylpyridine rubbers created a considerable amount of interest in the rubber industry. Compared to the 122° F butadiene/styrene copolymer then in use, butadiene/vinylpyridine copolymers displayed a superiority in several properties, notably tensile strength, tear resistance and resistance to cut growth. A number of terpolymers containing vinylpyridine type monomers were also investigated and these, with some exceptions, exhibited the same general advantages and disadvantages as the two-component copolymers.

Some difficulty was encountered in early polymerization of vinylpyridine copolymers on a large scale, chiefly in preflocculation and lack of proper control over polymer viscosity and conversion rates. These problems were lessened somewhat in the polymerization of three-monomer systems. Processing difficulties were also encountered arising from incompatibility of vinylpyridine copolymers with other rubbers and a high rate of cure resulting in scorching tendencies. Treadwear results of tires made with these rubbers were encouraging but again complications appeared in the form of tread separations and an excessive increase in hardness after use.

Because of the above-mentioned problems, together with the introduction of improved 41° F butadiene/styrene rubber, interest in these rubbers waned somewhat after World War II. More recently, however, interest in vinylpyridine rubbers has risen due to commercial availability of new monomers and the possibility of utilizing the reactivity of vinylpyridine polymers through new compounding techniques.

PYRIDINE MONOMERS

A considerable number of pyridine derivatives have been investigated as rubber monomers. A partial list of these, considered to be of most importance, is shown in Table I. Others in addition to those listed have been investigated to determine polymerization characteristics[1,4,7,9,11,21].

Of the compounds in Table I, 2-vinylpyridine and 2-methyl-5-vinylpyridine have been the chief ones used in large scale evaluations because of their availability. 2-Vinylpyridine is derived chiefly from coal tars produced during the

conversion of coal to coke. Commercial quantities of 2-methyl-5-vinylpyridine have been synthesized from petroleum raw materials.

BUTADIENE–VINYLPYRIDINE COPOLYMERS

Numerous investigations were conducted on the copolymerization of butadiene with vinylpyridine compounds under Office of Rubber Reserve sponsorship[9,11]. Although the first copolymers so produced were approximately equivalent to 122° F butadiene/styrene rubber (SBR 1000 type) in physical properties, further investigations showed advantages for the vinylpyridine copolymers in stress-strain properties and in resistance to cracking. In some instances the investigators also showed advantages in hysteresis and resilience properties. Because of availability and lower cost, a major portion of the work during this period was with 2-vinylpyridine. Various other monomers of the vinylpyridine type were studied during this time but, in general, none of these were considered superior to 2-vinylpyridine. Polymerization of the vinylpyridines under the government program were conducted for the most part in the Mutual recipe with slight modifications.

Table I

Pyridine Derivatives Investigated as Comonomers with Butadiene

Comonomer	Monomer ratios, butadiene/comonomer	References
2-Vinylpyridine	95/5 to 65/35	7, 9, 11, 30
3-Vinylpyridine	75/25	7
4-Vinylpyridine	75/25	7
2-Methyl-5-vinylpyridine	90/10 to 60/40	7, 25, 27, 31
2-Methyl-6-vinylpyridine	75/25	7
5-Ethyl-2-vinylpyridine	75/25	7, 31
2,4-Dimethyl-6-vinylpyridine	75/25	7
2-Methyl-5-cinnamoylpyridine	90/10 to 80/20	21

Interest created by the laboratory polymerizations led to production on a larger scale at the Government Pilot Plant of a 75/25 butadiene/2-vinylpyridine copolymer[12,23]. On the pilot plant scale, difficulty in polymerization was encountered with (a) formation of prefloc, (b) hard particles of polyvinylpyridine dispersed throughout the finished copolymer, (c) erratic conversion rates and (d) erratic Mooney viscosity. Further laboratory work showed these adverse conditions could be overcome for the most part by use of inhibitors and stabilizers, and by stricter control over process variables.

In 1948 Frank, Juve and coworkers published results on the copolymerization of several of the monomers listed in Table I with butadiene or isoprene.[7] Copolymers of commercially available 2-vinylpyridine had been shown to be superior to 122° F SBR in several respects; however, the potential supply of 2-vinylpyridine from coal tar picoline and formaldehyde was limited. Therefore, the investigation was undertaken to determine the suitability of various other vinyl-substituted pyridines as supplements for 2-vinylpyridine. Of these, 5-ethyl-2-vinylpyridine and 2-methyl-5-vinylpyridine were of particular interest since they can be synthesized from 5-ethyl-2-methylpyridine, readily prepared in turn from paraldehyde and ammonia[6,8].

Polymerizations were carried out in water emulsions at 122° F using the Mutual type recipe. Copolymerization rates with butadiene of the vinylpyridine monomers studied are shown in Table II in order of decreasing rate. These data are typical of the increased rate obtained with vinylpyridines as

TABLE II

COPOLYMERIZATION OF SUBSTITUTED VINYLPYRIDINES WITH BUTADIENE [7]

Monomer composition	Conversion after 8 hours, per cent
75/25 Butadiene/4-vinylpyridine	91.0
75/25 Butadiene/2-vinylpyridine	82.3
75/25 Butadiene/2-methyl-6-vinylpyridine	78.5
75/25 Butadiene/3-vinylpyridine	74.2
75/25 Butadiene/2-methyl-5-vinylpyridine	69.5
75/25 Butadiene/5-ethyl-2-vinylpyridine	66.5
75/25 Butadiene/styrene control (122° F SBR)	48.8
75/25 Butadiene/styrene control (122° F SBR)	78.2[a]

[a] Conversion after 12 hours.

compared to styrene in copolymerization with butadiene. Properties of butadiene copolymers with several of the substituted vinylpyridines were determined (Table III). These polymers were relatively tough in the crude state but gave no difficulty in mixing and handled nicly on a cold mill. The copolymers vulcanized at an appreciably higher rate than 122° F butadiene/styrene copolymer. Compared to the latter, several of the rubbers displayed high tensile strength and a high quality index. The quality index as used here represents the relative rating of a polymer with respect to its hysteresis characteristics and its resistance to crack growth during flexing. These were the tire tread properties

TABLE III

PROPERTIES OF VINYLPYRIDINE COPOLYMERS [7]

75/25 Butadiene/Vinylpyridine Monomer Ratio

Polymer	Vinylpyridine monomer	n-Dodecyl mercaptan, %	Time, hours	Conversion, %	Intrinsic viscosity
A	3-Vinylpyridine	0.5	8	78.8	1.15
B	5-Ethyl-2-vinylpyridine	0.5	11	83.6	2.12
C	2-Methyl-5-vinylpyridine	0.35	9	76.0	2.05
D	2-Methyl-6-vinylpyridine	0.5	7	71.0	1.91
E	2,4-Dimethyl-6-vinylpyridine	0.5	7½	84	—
F	122° F SBR Control (X-125)	—	—	—	—

Polymer	212° F Mooney, ML-4	Sulfur, % of copolymer	Cure, min. at 280° F	300% modulus, psi	Tensile, psi	Elongation, %	Heat build-up, °F	Perm. set, %	Shore A Hardness	Flex crack growth,[a] kc	Average quality index
A	88	1.0	75	1360	3780	593	66	13.6	59	480	5.5
B	—	1.75	30	1350	3050	550	155	47.1	—	1400	6.5
C	72	1.75	75	1920	3610	473	57	10.3	66	280	5.4
D	—	1.25	60	1050	3100	674	54	7.0	—	300	2.6
E	88	1.25	45	1190	2060	487	63	11.3	67	200	1.9
F	48	2.0	150	890	3380	620	52	9.4	60	210	2.5

Compounding Recipe

Copolymer	100
EPC black	50
Zinc oxide	5
Paraflux	5
Stearic acid	1.5
Santocure	1.2
Sulfur	variable

[a] Number of flexures required for an initial crack to grow to an arbitrary rating.

in which SBR was most deficient. However, the higher indexes exhibited by some of these polymers arise mostly from improved flex life as the heat buildup is high.

More recently, Marvel, Taft and coworkers[21] have reported on copolymerization with butadiene of a series of pyridine analogs of chalcone (benzalacetophenone) and cinnamic acid. This series included 2-pyridalacetophenone, 2-pyridal-*p*-chloroacetophenone, 3-pyridalacetophenone, 4-pyridalacetophenone, 2-cinnamoylpyridine, 2-methyl-5-cinnamoylpyridine, 4-cinnamoylpyridine and 2-pyridal-2′-acetylpyridine. Butadiene and 2-pyridal-*p*-aminoacetophenone did not form a copolymer. Work with copolymers of butadiene and benzalacetophenone had shown these imparted low heat build-up; poly-

TABLE IV

COPOLYMERS OF PYRIDINE DERIVATIVES OF CINNAMIC ACID AND DERIVATIVES[21]

Polymer	122° F SBR (X-720)	Ill. 332	Ill. 336	Ill. 337	Ill. 342
Comonomer with butadiene	Styrene	2-Pyridal-aceto-phenone	2-Methyl-5-cinnamoyl-pyridine	3-Pyridal-aceto-phenone	2-Methyl-5-cinnamoyl-pyridine
Monomer ratio in charge	71/29	85/15	85/15	90/10	85/15
Combined comonomer, %	—	25	14	17	15
Mooney (ML-4 at 212° F)	48	115	145	136	52
Stress-Strain at 77° F, Tread Type Recipe* (50 min. cure at 292° F)					
Tensile, psi	3810	3960	2610	2930	2780
Elongation, %	650	390	240	270	340
Stress-Strain at 77° F, Carcass Recipe** (40 min. cure at 280° F)					
300% Modulus, psi	450	280	960	640	380
Tensile, psi	1890	1550	1190	1050	1120
Elongation, %	650	780	330	410	580
Set, %	18	10	1	1	5
Goodrich Hysteresis Data, Carcass Recipe** (90 min. cure at 280° F)					
Temperature rise, ° F	25	127	11	20	22
Initial compression, %	30.2	45.3	24.0	28.4	32.1
Set, %	7.2	51.4	1.8	5.2	8.0
Shore A hardness	39	35	47	41	40

* Tread Recipe: Polymer 100, EPC black 40, zinc oxide 5, sulfur 2, 2,2-dithiobisbenzothiazole 1.75.
** Carcass Recipe: Polymer 100, HMF black 30, red lead 2.5, sulfur 2, Circosol 2XH 20, 2-2-dithiobisbenzothiazole 1.

merization of cinnamic acid and its derivatives and thiophene analogs of chalcone had also been studied. The work was extended to pyridine analogs of chalcone and cinnamic acid to determine if this would lead to improvements in the pyridine rubbers, particularly of hysteresis properties.

Polymers were made in the Mutual recipe with potassium persulfate as initiator and lauryl mercaptan as modifier. Studies of polymerization were also conducted with azobisisobutyronitrile as the initiator and in an acidic recipe as well as a solution recipe. The copolymers of 2-pyridalacetophenone, 3-pyridalacetophenone and 2-methyl-5-cinnamoylpyridine with butadiene (Mutual recipe at 122° F) were evaluated. Properties of these are shown in Table IV. The Mooney viscosity of these polymers was high. As the copolymer of butadiene and 2-methyl-5-cinnamoylpyridine possessed the most

interesting properties a lower Mooney sample of this rubber was prepared; properties of the latter are also shown in Table IV. High Mooney 2-methyl-5-cinnamoylpyridine copolymer with butadiene showed some promise as a low

TABLE V

EFFECT OF MONOMER RATIO ON PROPERTIES OF BUTADIENE/2-METHYL-5-VINYLPYRIDINE RUBBERS [27]

Monomer ratio	Combined methyl-vinyl-pyridine, %	300% modulus, psi	Tensile, psi	Elongation, %	Heat generation, °F	Resilience, %	Flex life, ke	Abrasion index, %	Mooney scorch at 280° F, min.
Tread Formulation									
90/10	8	1470	2500	435	81	57	4	124	—
85/15	12	1570	3100	470	76	63	4	127	8.5
80/20	18	1730	2710	510	68	74	12	170	11
75/25	21	1780	3470	480	71	62	13	160	12
70/30	24	2120	3675	470	70	62	9	167	9
60/40	31	2020	3225	440	75	58	17	190	10
SBR 1500	—	1300	3220	610	76	58	24	100	29

Monomer ratio	Combined methyl-vinyl-pyridine, %	300% modulus, psi	Tensile, psi	Elongation, %	Heat generation, °F	Flex life, ke	Gehman freeze point, °C
Carcass Formulation							
90/10	8	820	1400	440	43	3	—
85/15	12	830	2410	525	42	2	−60
80/20	18	830	3080	580	38	2	−52
75/25	21	770	2700	560	40	3	−52
70/30	24	975	2850	530	41	3	−49
60/40	31	1020	2850	540	45	5	−27
SBR 1500	—	570	3290	710	47	5	−42

Compounding Recipes

	Tread	Carcass
Elastomer	100	100
HAF black	50	25
Zinc oxide	3	3
Stearic acid	1	1
Flexamine	1	—
Sulfur	1.75	2.5
Circosol 2XH	2.5	5
Paraflux 2016	2.5	5
Philcure 113	variable	variable
AgeRite Resin D	—	1
Staybelite resin	—	2.5
Diphenylguanidine	—	variable

Cure—30 minutes at 307° F

hysteresis rubber; however, when prepared to a comparable Mooney viscosity the heat generation was not appreciably better than for 122° F SBR (X-720).

Effect of monomer ratio.—Much of the work with vinylpyridine polymers was conducted with a monomer ratio of approximately 75/25 butadiene to comonomer. However, several investigations were also made of the effect of

variable monomer ratios. A study of the effect of monomer ratio on dynamic properties of butadiene-2-vinylpyridine copolymers showed the following trends as the vinylpyridine content[2] was increased from 5 to 35 parts: (a) tensile strength and modulus increased, (b) resilience at room temperature decreased, (c) resilience at 212° F was equivalent for 85/15, 75/25, and 65/35 copolymers and higher than for 122° F SBR, (d) hysteresis at 280° F decreased and (e) 65/35 and 75/25 copolymers of butadiene and 2-vinylpyridine possessed superior cut growth resistance compared to the 85/15 copolymer and 122° F SBR.

TABLE VI

PROPERTIES OF 85/15 AND 75/25 BUTADIENE/2-METHYL-5-VINYLPYRIDINE RUBBER-TREAD FORMULATION [22]

80° F										
300% modulus, psi	Tensile, psi	Elongation, %	200° F tensile, psi	Heat generation, ° F	Resilience, %	Flex life, kc	Gehman freeze point, ° C	Shore A hardness	212° F compounded Mooney, (MS-1½)	280° F Mooney scorch, min.
85/15 Butadiene/2-Methyl-5-Vinylpyridine										
1860	3020	435	1230	59	62	4	−67	62.5	33	19.5
75/25 Butadiene/2-Methyl-5-Vinylpyridine										
1820	3325	500	1390	62	59	14	−53	63.5	28	18.5
SBR 1500										
1250	3370	620	1660	65	62	14	−48	59	33.5	22.5

Compounding Recipe

	Butadiene/methylvinyl pyridine	Butadiene/styrene (SBR 1500)
Elastomer	100	100
HAF black	50	50
Zinc oxide	3	3
Stearic acid	1	1
Flexamine	1	1
Circosol 2XH	5	5
Paraflux 2016	5	5
Sulfur	1	1.75
Sulfasan R	1.5	—
NOBS Special	0.75	—
Santocure	—	1.1

Cure—30 minutes at 307° F

Copolymers with charge ratios of butadiene to 2-methyl-5-vinylpyridine of 90/10 to 60/40 were compared in both tread and carcass type formulations[27]. Selected results obtained with these rubbers and a standard 41° F butadiene/styrene rubber are listed in Table V. In these studies charge ratios of 80/20 to 70/30 of butadiene to 2-methyl-5-vinylpyridine appeared optimum from the standpoint of stress-strain and hysteresis properties. Higher modulus values and poorer low-temperature properties are evident with increasing amounts of combined pypridine monomer. All of the experimental compounds possessed poor scorch resistance. Good laboratory abrasion resistance was exhibited by all of the 2-methyl-5-vinylpyridine copolymers and those containing 18 per cent or more combined 2-methyl-5-vinylpyridine were particularly outstanding in this respect.

Methylvinylpyridine rubbers for general use.—Commercial quantities of 2-methyl-5-vinylpyridine became available in 1952 through synthesis from petroleum raw materials[5]. Basic raw materials are acetaldeyhde and ammonia. Methylethylpyridine is prepared by reaction of paraldehyde with ammonia and is subsequently dehydrogenated to methylvinylpyridine. Availability of this chemical gave impetus to its use as a rubber monomer and copolymers of 85/15 and 75/25 ratios of butadiene/2-methyl-5-vinylpyridine are now available in commercial quantities. These are prepared in existing copolymer plant facilities used for the production of butadiene/styrene types using a modification of a conventional SBR polymerization recipe.

TABLE VII

PROPERTIES OF 85/15 AND 75/25 BUTADIENE/2-METHYL-5-VINYLPYRIDINE RUBBERS–CARCASS FORMULATION [27]

80° F								
300% modulus, psi	Tensile, psi	Elongation, %	200° F tensile, psi	Heat generation ° F	Resilience, %	Blowout, min.	Shore A hardness	280° F Mooney scorch, min.
85/15 Butadiene/2-Methyl-5-Vinylpyridine								
1100	1700	380	420	33	75	30	55	20
75/25 Butadiene/2-Methyl-5-Vinylpyridine								
1050	2400	475	480	26	73	30	55.5	19
SBR 1500								
780	2790	590	700	38	76	20	53.5	12.5

Compounding Recipe

	Butadiene methylvinyl-pyridine	Butadiene styrene (SBR 1500)
Elastomer	100	100
HAF black	25	25
Zinc oxide	3	3
Stearic acid	1	1
Paraflux 2016	5	5
AgeRite Resin D	1	1
Staybelite resin	2.5	2.5
Sulfur	1.5	2.5
Sulfasan R	1.5	—
NOBS Special	1.25	—
Santocure	—	1.0
A-32	—	0.2

A difficulty in the use of the vinylpyridine derived rubbers has been the tendency toward prevulcanization or scorch. The scorch resistance of the majority of copolymers was marginal, presenting a problem in factory processing. Railsback and Biard[27] published data on the study of various curative systems for copolymers of butadiene and 2-methyl-5-vinylpyridine leading to formulations of increased processing safety. Numerous accelerator types, as well as variations in sulfur level, were studied; however, none of these combinations provided acceptable processing safety. Further study showed use of a sulfur donor in conjunction with a reduced sulfur level and a delayed action type of accelerator lengthened the scorch resistance. In this curative system a sulfur donor, such as 4,4′-dithiomorpholine, provided satisfactory processing

safety and a tight cure. Properties of 85/15 and 75/25 copolymers vulcanized with this type of system are shown in Tables VI and VII. In either the tread or carcass formulation these rubbers displayed higher modulus and slightly better heat buildup characteristics than a 41° F butadiene/styrene copolymer (SBR-1500).

Freeze resistance, particularly of the 85/15 copolymer, was superior to SBR 1500. Tensile strength at elevated temperature (200° F) and extrusion characteristics were poorer than for "cold rubber". From consideration of these

TABLE VIII

PROPERTIES OF MINERAL PIGMENT–REINFORCED BUTADIENE/2-METHYL-5-VINYLPYRIDINE COPOLYMER [27]

Filler	300% modulus, psi	Tensile, psi	Elongation, %	Heat generation, ° F	Resilience, %	Flex life, ke	Shore A hardness	Abrasion loss, cc	Compounded Mooney 212° F, MS-1½	Mooney scorch, 280° F, min.
75/25 Butadiene/2-Methyl-5-Vinylpyridine Copolymer										
Silica	1530	3620	560	53	67	9	70.5	6.6	64	16
Clay	1240	1940	480	41	69	15	58.5	32.4	23.5	18.5
HAF black	1830	3210	440	63	58	8	64	2.2	27.5	18
41° F Butadiene/Styrene Copolymer (SBR 1500)										
Silica	450	2775	690	79	52	9	73	23.3	78.5	18
Clay	500	2320	620	59	63	6	59	57.6	23.5	10
HAF black	1250	3320	590	61	61	17	59.5	7.1	34.5	22

Compounding Recipes

	Butadiene/2-Methyl-5-vinylpyridine		SBR 1500	
Elastomer	100	100	100	100
Mineral pigment	variable[a]	—	variable[a]	—
HAF black	—	50	—	50
Zinc oxide	3	3	3	1
Stearic acid	1	1	3	1
Flexamine	1	1	1	1
Philrich 5	10	10	10	10
Sulfur	1.5	1	3	1.75
Sulfasan R	1.5	1.5	—	—
NOBS Special	1.25	0.75	—	—
Altax	—	—	0.75	—
DOTG	—	—	1.5	—
Triethanolamine	—	—	1.0	—
Santocure	—	—	—	1.1

Cure—30 minutes at 307° F

[a] Adjusted to obtain a volume loading of 27.8 phr.

data it would appear that for tire tread stocks, a superiority in treadwear resistance would be necessary to justify use of the vinylpyridine-containing rubbers. The methylvinylpyridine rubbers do indeed show outstanding abrasion resistance in laboratory tests but have not been thoroughly proved in actual service.

Reinforcement by mineral pigments.—A rather unique characteristic of the butadiene/vinylpyridine copolymers is the high degree of reinforcement realized with clay and silica pigments in comparison to the reinforcement of butadiene-styrene rubber by these mineral pigments[24,27]. Most rubbers require high

curative levels for adequate vulcanization of mineral pigment loaded stocks and even then modulus is usually quite low. Vinylpyridine-derived rubbers reinforced with mineral pigments give high moduli, approaching those of black loaded stocks at equivalent volume loadings. The vinylpyridine-derived rubbers with clay, silica or other inorganic pigments are further marked by low heat generation and high resilience. These stocks have also shown excellent abrasion resistance on a laboratory scale. Preliminary road test results have indicated slightly better treadwear resistance for a silica reinforced 75/25 butadiene/2-methyl-5-vinylpyridine stock than for the same rubber or a butadiene/styrene copolymer compounded with 50 phr HAF black. Data illustrative of these properties, taken from the above references, are shown in Tables VIII and IX.

TABLE IX

PROPERTIES OF CLAY AND ZINC OXIDE–LOADED BUTADIENE/2-VINYLPYRIDINE COPOLYMER[24]

Filler	77° F 300% modulus, psi	77° F tensile, psi	77° F elongation, %	205° F tensile, psi	Heat generation, °F	Resilience, %	Flex crack growth, 0.001 in./kc	77° F hardness	Compounded Mooney, ML-4
75/25 Butadiene/2-Vinylpyridine Copolymer (XP-3)									
Clay	1300	1420	383	815	77	51	.06	61	63
Zinc oxide	350	1100[a]	540	245	40	51	0.1	53	50
Standard SBR 1000 (122° F Butadiene Styrene)									
Clay	420	950[a]	710	240	198	46	0.1	56	60
Zinc oxide	90	850	1070	130	180	47	None	37	47

Compounding Recipes

	Clay		Zinc oxide	
	XP-3	SBR 1000	XP-3	SBR 1000
Polymer	100	100	100	100
Zinc oxide	5	5	100	100
Clay	100	100	—	1
Softener (BRT No. 7)	5	5	5	5
Sulfur	2	2	2	2
Mercaptobenzothiazole	0.2	1.6	0.2	1.6

Cure—60 minutes at 292° F

[a] Estimated from other values in reference.

Oil-resistant properties.—Copolymers of butadiene and 2-methyl-5-vinylpyridine may also be rendered oil resistant by reaction with quaternizing agents. Reynolds, Pritchard, Opheim and Kraus[25,28] showed that compounding of these polymers with an active organic halide in addition to the ordinary pigments and curatives yields a vulcanized polymeric quaternary salt having good oil resistance. The quaternized rubbers obtained are resistant to a wide range of solvents including water, alcohols, aldehydes, ketones and esters as well as aromatic and aliphatic hydrocarbons. In addition to solid rubbery polymers suitable for fabrication of gaskets, O-rings and the like, it was observed that liquid copolymers could be converted into semisolid jellies, soft rubbers or hard resins through quaternization.

Since liquid polybutadiene and polybutadiene rubber do not exhibit changes in properties when treated with organic halides under the conditions used with the vinylpyridine polymers, it is believed the observed changes are associated with quaternization of the pyridine nitrogen. The quaternizing agents are not removed by extraction with solvents.

As in the cases noted above, the optimum tensile strength was obtained with 80/20 to 70/20 copolymers of butadiene and 2-methyl-5-vinylpyridine[21]. Oil resistance increased as the 2-methyl-5-vinylpyridine content increased. Freeze resistance is better for copolymers of lower methylvinylpyridine content; thus an 85/15 copolymer exhibits moderate oil resistance coupled with a low freeze point. 2-Methyl-5-vinylpyridine was found to be a better monomer for this type of oil resistant rubber than 2-vinyl-5-ethylpyridine.

ISOPRENE–VINYLPYRIDINE COPOLYMERS

Work reported on the copolymerization of vinylpyridine with isoprene does not indicate any advantage over comparable rubbers prepared with butadiene[3,7,22]. Many of the properties of isoprene copolymers were somewhat similar to those of butadiene/vinylpyridine copolymers but were inferior in other respects. The rate of copolymerization of vinylpyridines with isoprene was shown by several investigators to be lower than with butadiene. Likewise the isoprene copolymers were shown to cure faster than the butadiene counterparts. Another property noted for the isoprene/vinylpyridine rubbers was a pronounced tendency toward reversion similar to that of natural rubber. This latter tendency is in contrast to the hardening encountered with aging of the vinylpyridine/butadiene rubbers and was of some interest with regard to overcoming the embrittlement of butadiene/vinylpyridine rubbers by combination of the two types.

TERPOLYMERS

Terpolymers of vinylpyridine with other monomers that have been investigated include the following:

Butadiene/styrene/vinylpyridine
Butadiene/isoprene/2-vinylpyridine
Butadiene/dichlorostyrene/2-vinylpyridine
Butadiene/α-methylstyrene/2-vinylpyridine
Butadiene/acrylonitrile/2-methyl-5-vinylpyridine

Because of the higher cost of vinylpyridine monomers relative to styrene, a number of investigations were made in which the styrene in an SBR type polymer was only partially replaced by a vinylpyridine monomer. In a comprehensive study covering the range of 75/25/0 to 75/0/25 butadiene/styrene/2-vinylpyridine in increments[24] it was found that a 75/15/10 butadiene/styrene/2-vinylpyridine terpolymer offered the best balance between properties and cost.

Pilot plant quantities of a 72/18/10 butadiene/styrene/vinylpyridine terpolymer were produced in the Government Pilot Plant. Some problems were encountered with preflocculation and control of Mooney viscosity but these were overcome[12]. Physical tests on this polymer in comparison to 122° F SBR showed significantly higher tensile and slightly better elongation with comparable modulus and set values. The flex life-heat rise balance, rebound and Shore hardness were equivalent to 122° F SBR.

Rinne and Rose published data on butadiene/styrene/vinylpyridine terpolymers also prepared on a pilot plant scale[20]. These exhibited superior quality and equivalent processing characteristics in comparison to the SBR type controls. Replacement of styrene with 2.5 to 5 parts of 2-vinylpyridine on an

equal weight basis resulted in notable improvements in tensile strength, rebound, flex crack resistance, aging and cure stability. These terpolymers showed excellent milling behavior, rapid breakdown and increased raw tack. The terpolymers were suggested for specialty applications where improved flex crack and aging resistance are important. Based on results up to that time, use of the vinylpyridine terpolymers in tires was not recommended, primarily because of incompatibility with SBR or natural rubber. Tires were prepared with 70/20/5 butadiene/styrene/2-vinylpyridine terpolymer as a tread stock; however, separation of the tread and carcass occurred under test conditions of only short duration.

The rate of copolymerization of butadiene, isoprene and vinylpyridine decreased progressively as more isoprene was substituted for butadiene[22]. These terpolymers all contained 25 parts 2-vinylpyridine with the balance either butadiene or isoprene or both. The replacement of an equivalent amount of butadiene with 10, 25 or 50 parts isoprene decreased the tensile strength as more isoprene was used. Modulus and hysteresis values of the terpolymers varied erratically. At room temperature, increased amounts of isoprene lowered the rebound but increased rebound when this property was measured at 212° F.

Early work with a 66/21/13 butadiene/dichlorostyrene/vinylpyridine terpolymer yielded high modulus and a very high tensile strength. Subsequent polymers made in 5-gallon reactors to 18–70 Mooney viscosity (ML-4) were equal or superior to SBR in processing (milling, extrusion and breakdown), tensile strength, elongation and flex life-heat generation balance. Low temperature properties were inferior to SBR. Modulus and hysteresis values were generally higher[22].

As both butadiene/α-methylstyrene and butadiene/styrene/2-vinylpyridine copolymers were indicated to be superior to SBR in certain respects, an attempt was made to combine the good properties of these by making a terpolymer containing butadiene, α-methylstyrene and 2-vinylpyridine[10]. Polymers were prepared with monomer ratios (in the order above) of 72/23/5, 72/18/10 and 72/13/15. All of the polymers possessed slightly more tack than SBR but milling properties were similar. The polymers exhibited higher modulus and slightly higher tensile strength than SBR controls. The principal advantage noted for the terpolymers was a significant improvement in tear resistance.

Terpolymers of butadiene/acrylonitrile/2-methyl-5-vinylpyridine have been studied as oil resistant rubbers[21]. When quaternized with an organic halide these terpolymers are more oil resistant than the two component butadiene/methylvinylpyridine polymers. In many solvents these are better than butadiene/acrylonitrile copolymers and approach the properties of the latter type rubber containing high amounts (35–40 per cent) of acrylonitrile, particularly in such solvents as diester lubricants. An interesting property of the quaternized terpolymer is the excellent resistance to blowout at elevated temperatures under severe dynamic conditions.

MISCELLANEOUS APPLICATIONS

Latexes containing vinylpyridine constituents, such as 2-vinylpyridine, are effectively employed in cord dip formulations for the tire industry. This type of cord dip has been particularly successful in improving adhesion between rubber and synthetic fibers. Consumption of vinylpyridine-containing cord dip is expected to rise rather rapidly in the next few years following an antici-

pated trend of increased use of nylon for tire cord. Copolymers containing vinylpyridine or vinylpyridine derivatives appear useful for other adhesive applications due to their polar nature and reactivity. This is especially true of the substituted vinylpyridines. Strong adhesives for the bonding of rubbers, metals and other materials have been obtained using epoxy resins as curatives. The rubber can also be cured with phenolic or epoxy resins as the sole curative in carcass and tread type recipes to yield stocks with a good balance of physical properties.

Polymers and copolymers derived from vinylpyridines can be used as emulsifiers for acid polymerization of styrene, butadiene, acrylonitrile and other monomers[26]. These polymeric emulsifiers yield fast polymerization systems yet provide polymers which are relatively free of nonpolymeric materials.

CONCLUSIONS

In appraisal of the copolymers containing vinylpyridines and vinylpyridine derivatives, two broad fields of application are considered: (a) specialty applications, including oil-resistant stocks, cord dips and adhesives and (b) general purpose rubber, including primarily tread and carcass compounds for tires.

The quaternized copolymers or terpolymers provide good oil and solvent resistance as a whole and are outstanding in resistance to some specific types of fluids. For general overall oil resistance, these rubbers approach butadiene/acrylonitrile copolymers of high (35–40 per cent) acrylonitrile content. Copolymers of low vinylpyridine content provide a useful combination of oil resistance and good low temperature properties. The quaternization reaction which occurs with these rubbers is worthy of additional study. Usefulness of vinylpyridine copolymers in cord dips has been proven and this application will undoubtedly become more important. Vinylpyridine-containing copolymers and terpolymers with acrylonitrile as the third monomer show considerable promise in adhesive formulations.

The possibility of greatly improved treadwear is the most important factor in continued study of vinylpyridine-type rubbers. Tire test results have been erratic ranging from significant increases in treadwear to none. Unpublished data on recent tests of butadiene copolymers containing only about 5 per cent 2-methyl-5-vinylpyridine have shown 20 to 25 per cent improvement in treadwear over butadiene/styrene rubber (SBR 1500). Treadwear ratings of 150 per cent and greater, based on 41° F butadiene/styrene rubber at 100 per cent, are reputed for copolymers containing larger amounts of vinylpyridine monomers. If these potentials can be realized, and processing and fabrication problems overcome, it can be expected that vinylpyridine copolymers will receive rapid and widespread acceptance for use in tires and other large-volume applications.

OTHER RUBBERS CONTAINING BASIC CONSTITUENTS

Monomers of a basic character, other than vinylpyridines and their derivatives, have been prepared with some success[4,9,11] although none have been investigated on a scale comparable to the vinylpyridine types. Copolymerization characteristics of 2-vinylquinoline with butadiene were studied by Bachman and Micucci[1] and Marvel and coworkers[16,18]. The resulting polymers appeared to be of good quality but the polymerization reactions were slow.

Conversions of the order of 30 per cent were obtained in 12 to 20 hours with a 75/25 monomer ratio of butadiene to 2-vinylquinoline in emulsion polymerization systems. Rinne[29] reported 39 per cent conversion of a 72/18/10 charge ratio of butadiene/styrene/2-vinylquinoline. The terpolymer possessed better milling properties than 122° F SBR and was fast curing. Tensile strength of the latter polymer was low and elongation was slightly better than for butadiene/styrene rubber. An attempted copolymerization of 1-vinyl-2,5-dimethylpyrrole[19] was unsuccessful possibly due to inhibition by impurities.

Marvel and coworkers prepared a number of amino substituted compounds as monomers for synthetic rubber including β-dimethylaminoethyl acetate[20], *p*-N,N-dimethylaminostyrene[14,15,18], α-(N,N-methylphenylamino) styrene[17] and *p*-dimethylaminostyrene[18]. The latter two aminostyrenes did not copolymerize with butadiene under the conditions used. Copolymerization of 75/25 ratio of butadiene and *p*-N,N-dimethylaminostyrene yielded a sticky polymer in 30 per cent conversion.

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THE CHEMISTRY OF CARBON BLACK AND REINFORCEMENT

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I. INTRODUCTION

Carbon black contributes so much to the desirable properties of vulcanized rubber that it is almost a universal compounding ingredient for quality stocks. (For earlier reviews, see Reference 1.) The function of carbon black in rubber is commonly referred to as reinforcement, and numerous attempts have been made to identify reinforcement with one or more specific physical properties of the vulcanizate. However, such attempts are almost certain to be doomed to failure. To convey the generally accepted meaning of reinforcement, it is necessary to define it in terms of properties of *use*. One general definition seems applicable; namely, *reinforcement is the enhancement of one or more properties of an elastomer by the incorporation of some ingredient, thus making it more suitable for a given application*. This definition has evolved in the rubber industry because of our inability to identify the phenomenon of reinforcement with any readily measurable physical or chemical properties of a rubber compound. In practice we speak of reinforcing pigments, or reinforcing resins, as distinct from the elastomer, curing ingredients, softeners, antioxidants, etc. To a tire compounder, a reinforcing material is one which, when incorporated into his compounds, will result in a tire which will wear better on the road. To a v-belt manufacturer, the reinforcing material will give longer service life to his product. The definition is so general that it includes fabrics, wire, etc., when these can be used to give longer service life to the manufactured item. In this paper the discussion will be centered on the group of important reinforcing materials which are called carbon black(s).

A search of the literature impresses one with the fact that most serious studies of reinforcement have employed physical or mathematical methods almost exclusively. The chemist may study carbon black as such, but his attempts to extend his work to the field of reinforcement have shown slight success. On the other hand, all too frequently the physical or mathematical studies have either been based on incomplete, questionable or, at best, unproved assumptions—or these have been introduced into the argument "by way of the cellar window."

It is quite possible to determine a number of properties of various carbon blacks and make empirical correlations with physical properties, and even with use-properties of rubber stocks which contain them[2]. One is tempted to feel that there must be some basic reasons for such correlations—some underlying principles. Unfortunately, such procedure is frought with many uncertainties. Correlations of this type can be made with various sets of carbon black properties, and it is not always certain which ones, if any, are really responsible for the changes in rubber properties which we observe.

In this review the preparation of carbon blacks and their properties will be discussed: Then an attempt will be made to set out certain observations which seem to have significance in the general problem of just what takes place when rubber is vulcanized in the presence of carbon black. *The approach is that of a chemist.* It is recognized that the study of reinforcement by physical methods

TABLE I

TRADEMARKS OF RUBBER-GRADE CARBON BLACKS MANUFACTURED IN THE USA[1]

Process	Furnace								
Basic feed stock	Oil						Gas		
Type of Rubber-Grade Carbon Black / Manufacturer	Super Abrasion Furnace	Conducting Furnace	Intermediate Super Abrasion Furnace	High Abrasion Furnace	Fast Extrusion Furnace	General Purpose Furnace[2]	Fine Furnace	High Modulus Furnace	Semi-Reinforcing Furnace[3]
Phillips Chemical Company	Philblack E		Philblack I	Philblack O	Philblack A				
Columbian Carbon Company	Statex 160		Statex 125	Statex R	Statex M	Statex G	Statex B	Statex 93	Furnex
Cabot Carbon Co.[4]	Vulcan 9	Vulcan C Vulcan SC Vulcan XC-72	Vulcan 6	Vulcan 3	Sterling SO	Sterling V	Sterling 99	Sterling L	Sterling S[3] Pelletex
J. M. Huber Corporation		Aromex CF	Aromex ISAF	Aromex HAF	Arovel FEF	Arogen GPF		Modulex HMF	Essex SRF[3]
Sid Richardson Carbon Company									
United Carbon Company	Kosmos 85	Kosmos CF	Kosmos 70	Kosmos 60	Kosmos 50	Kosmos 35		Kosmos 40	Kosmos 20
Thermatomic Carbon Company[5]									
Continental Carbon Company[6]		Continex CF	Continex ISAF	Continex HAF	Continex FEF			Continex HMF	Continex SRF

[1] All of the carbon blacks in this table are manufactured in the USA. Some of these brands are also manufactured in plants outside the USA. Shawinigan acetylene black, which is mentioned frequently in this paper, is manufactured by Shawinigan Products Corporation at Shawinigan Falls, Quebec, Canada. It is used in limited quantities in the USA.

[2] May be made from oil or a mixture of oil and gas.

[3] There are five types of SRF black manufactured and sold to the rubber industry. The following lists the types and brands manufactured in each classification as on the basis of the information available to the author. They are classified by relative staining qualities and modulus. High modulus types are also known as No. 3 types, named after the #3 unit of the General Atlas Carbon Company Pampa Plant which produced this type of carbon black.

Staining	*Modulus*	*Designation*
Regular	Regular	Kosmos 20, Sterling S, Essex SRF, Furnex
Non-Staining	Regular	Sterling NS, Essex-SRF-NS
Regular	High	Kosmos 20-HM, Pelletex, Essex SRF No. 3
Non-Staining	High	Pelletex NS, Essex-SRF #3-NS, Continex SRF
Especially Non-Staining	High	Pelletex X-Clear

TABLE I—(*Continued*)

Process	Thermal		Channel				
Basic feed stock	Gas		Gas				
Type of Rubber-Grade Carbon Black / Manufacturer	Fine Thermal	Medium Thermal	Easy Processing Channel	Medium Processing Channel	Hard[7] Processing Channel	Conducting Channel	Special Surface-treated Channel
Phillips Chemical Company							
Columbian Carbon Company			Micronex W-6	Micronex Standard	Micronex Mark II		
Cabot Carbon Company	Sterling FT	Sterling MT Sterling MT-NS	Spheron 9	Spheron 6	Spheron 4	Spheron C	
J. M. Huber Corporation			Wyex EPC	Arrow TX-MPC			
Sid Richardson Carbon Company			Texas E	Texas M			Texas 109
United Carbon Company			Kosmobile 77[4]	Kosmobile HM[5]	Kosmobile S[5]	Kosmos BB[5] Voltex	
Thermatomic Carbon Company	P-33	Thermax Thermax-Stainless					
Continental Carbon Company			Continental AA (Witco No. 12)	Continental A (Witco No. 1)	Continental F (Witco No. 6)	Continental R-40	

Note [3] continued. Both staining and modulus are relative properties. Non-staining types are generally non-staining to white side wall stocks in service. Regular types would be staining in such an application due to colored extractable matter in appreciable quantities. Pelletex X-Clear is made for a few applications requiring the practical limit of freedom from staining properties. These designations are made by purchasers and may or may not be considered as actual trademarks by the manufacturer. NS refers to non-staining. HM and #3 refer to high modulus types.

[4] Distributed by Godfrey L. Cabot, Inc.
[5] Distributed by R. T. Vanderbilt Company.
[6] Distributed by Witco Chemical Company.
[7] Only very minor amounts of HPC black are sold to the rubber industry at the present time. Some manufacturers feel that the classification should be discontinued.
[8] These types of carbon black are also marked in the export market under other trademarks.

EPC—Dixidensed 77 and Atlantic E-42
MPC—Dixidensed HM and Atlantic 95
HPC—Atlantic 98
CC—Dixie BB

is of tremendous importance. Both approaches are necessary to make a well-rounded description of the phenomena involved. However, the chemical side has been largely neglected; and the author desires to summarize the available information, adding some new data which seem pertinent when they are available, to bring the chemical side of the picture into focus. It is hoped that a review article covering the excellent physical studies of Blanchard[3], Mullins[4], Greensmith[5], Schallamach[6], Kraus[7] and others will be prepared in the near future and that the whole subject can be brought into better perspective at a later date.

II. TYPES OF CARBON BLACK AND THEIR MANUFACTURE

In this section only those rubber-grade carbon blacks which are manufactured in the USA and in Canada will be discussed. Aside from the German carbon black, CK-4, they include all of the large volume carbon blacks used by the rubber industry outside the Iron Curtain countries. A number of the brands or types which are manufactured in the USA are available from carbon black plants in England, Wales, France and Germany.

The rubber-grade carbon blacks can be grouped according to the processes by which they are manufactured as follows:

(1) Channel blacks
(2) Gas furnace blacks
(3) Oil furnace blacks
(4) Thermal blacks
(5) Acetylene black

With the exception of acetylene black, all commercially available carbon blacks are made from natural gas, oil or a mixture of the two. It is conceivable that carbon black could be made from many other materials; but, at present, economic and technological factors limit the choice of raw materials to natural gas and oil except for the specially conducting, premium priced acetylene black.

Basically, carbon black is produced by subjecting a hydrocarbon-rich fuel to pyrolysis. The hydrocarbon is cracked to carbon black, hydrogen and minor amounts of tarry materials. If natural gas is the raw material and if no combustion takes place, a thermal black is produced. If acetylene is the raw material, the product is acetylene black. However, most carbon blacks are formed by conducting the pyrolysis in a flame or by subjecting it to a flame after the beginning of the pyrolysis. Under these conditions, much of the hydrogen and tarry materials are oxidized to water and oxides of carbon. These products are blended with the water, carbon monoxide and carbon dioxide formed by combustion of the fuel. The choice of fuel and the conditions under which the pyrolysis and combustion take place determine the type of carbon produced.

A. CLASSIFICATION OF RUBBER-GRADE CARBON BLACKS

In the United States fifteen major types of carbon black are manufactured for the rubber industry. The acetylene black made in Canada increases the list of carbons used in rubber to sixteen. Table I is an attempt to list all brands of carbon black manufactured in the USA and Canada according to the generally accepted classification of these materials, their manufacturers and suppliers. The specially surface-treated channel black, Texas 109, is included for completeness although only minor amounts of this material are consumed by the

rubber industry, mainly in mechanical goods. It does not seem to warrant a separate classification at this writing. The classification was first set up by the War Production Board[8], but has been modified over the years to make it more realistic. Such a classification is of necessity somewhat arbitrary. To illustrate this, one can cite Statex 93 which is not interchangeable with the other HMF blacks—it imparts to rubber a higher modulus and more reinforcement than the remaining HMF's.

Further, whenever a new type of carbon black is produced, some jockeying of quality usually takes place. At such times various suppliers offer products of the new type which may not be interchangeable. Competition then reduces the differences between the new competitive products until a measure of uniformity is attained. It may happen that a real market develops for two types of carbon black which are considered to be in the same classification. Then a new classification may be necessary. At the present writing two distinct types

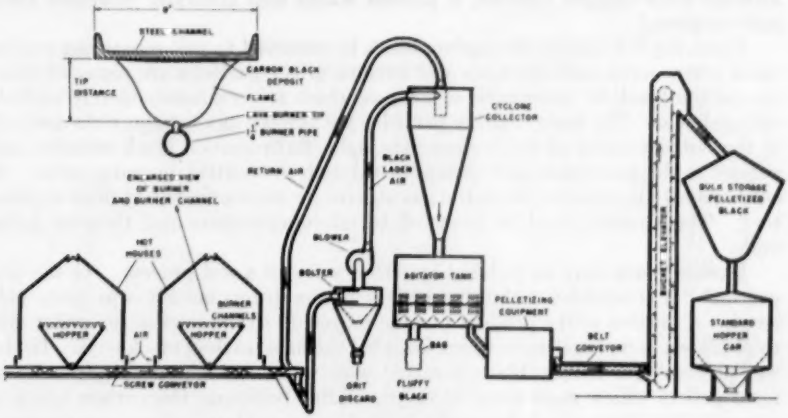


FIG. 1.—Flow sheet of process for making channel black. (Courtesy of Interscience Encyclopedia, Inc., New York[12].)

of ISAF are being produced, the so-called "high modulus ISAF" and "low modulus ISAF". These products are not interchangeable, and it is not possible to determine at this time whether the industry will standardize on one of these types or whether both types will be manufactured. In this latter case, it will be necessary to set up a new classification.

B. THE MANUFACTURE OF RUBBER-GRADE CARBON BLACKS

1. The channel process (cf. Figure 1).—In the channel process, natural gas is burned in small flames which impinge and deposit carbon on 8 to 10-inch channel irons, from which the process derives its name. The natural gas is fed to lava burner tips at the rate of about 2 to 3 cu ft per hour. The distance between the burner tips and the channel irons is in the neighborhood of 2 to 4 inches and must be carefully controlled since this is one of the critical factors in determining both quality and yield. The channel irons upon which the flames impinge and deposit carbon move slowly back and forth across stationary scrapers which cause the deposited carbon black to fall into hoppers and thence

into screw conveyors which convey it to the grit separating equipment. The whole operation is conducted in sheet iron "hot houses" which are provided with draft openings at the bottom and outlets for the combustion products at the top. These hot houses are generally 100 to 200 feet long, 8 to 14 feet wide and 9 to 14 feet high. They contain 6 to 12 channel irons upon which the flames impinge. Several thousand flames are burned in each hot house to produce several hundred pounds of channel black per hot house per day. A large channel black plant will contain several hundred hot houses arranged in units of 30 to 100 hot houses each.

The quality of the channel black is determined by a balance of many factors including tip spacing, tip to channel distance, gas rate per tip, gas quality, tip design and drafting. In general, a long, lazy, cool flame tends to produce easy processing channel black. Hot, short flames produce harder processing channel blacks or color blacks. (Many color blacks are subjected to after treatment to increase their oxygen content, a process which also generally increases their surface areas.)

From the hot houses the carbon black is conveyed to grit separating equipment where hard, carbonaceous and ferrous, gritty particles are removed from the carbon black by pneumatic separators which are commonly merely inefficient cyclones. The heavy, gritty particles are thrown against the walls and fall to the bottom outlet of the cyclone; the light, fluffy carbon black remains suspended in the gas stream and passes out through the central discharge tube. It subsequently is removed from the gas stream by more efficient cyclone separators. The channel black is next fed to micropulverizers and then to pellet mills.

Carbon black may be pelleted by either a dry or a wet process. In the dry process[9,10] it is tumbled with other pellets in long drums until it is properly pelleted. A portion of the product may be recycled[10] to the inlet of the pellet mill to provide a bed of pellets to which is added the loose carbon black feed. In the wet process[11] the carbon black is mixed with water in high speed pug mills to form pellets which must then be dried. After pelleting, the carbon black is stored in bins from which it may be bagged or loaded into hopper cars for shipment in bulk.

An excellent description of the channel process is contained in an article by W. R. Smith[12]. In addition, several more recent technological developments are described in the patent literature[13].

2. The furnace process (*cf. Figure 2*).—In the furnace process, oil, gas or a mixture of the two is burned in refractory-lined furnaces with a deficiency of air. The choice of fuel, the design of the furnace, the burner system and the operating conditions (air rate, fuel rate, preheat temperature, etc.) are critical factors in determining and in controlling the quality of the product. A variety of furnace and burner designs by which carbon black can be produced are described in the patent literature. A description of one process was published recently[14]: "The Philblack process is carried out by combustion and thermal decomposition of a hydrocarbon oil being fed continuously into a reactor furnace with a limited supply of air. The limited supply of air, and in some cases the combustion fuel, is admitted tangentially to the tubular-shaped reactor in such a manner that a "whirling" or "cyclonic" flow is imparted. This cyclonic flow, with the combustion of the fuel, forms a blanket of flame and combustion products along the reactor walls that extend from the combustion section into the reaction tunnel. The conversion-oil vapor is introduced axially to the reactor, and initially, at least, forms the nonrotating central core or "eye" of

the cyclonic flow. It is conceived that the thermal decomposition of conversion oil occurs in the central core. Carbon black, gaseous by-products and water vapor are formed from the combustion and decomposition reactions. . . . The reactor products are quenched by direct water sprays as the gases egress from the reactor to reduce the temperature and stop the reaction. . . ." After the carbon black-laden gas emerges from the reactor or furnace, its temperature is suitably adjusted by open water sprays before entering the collecting system. For many years, the collecting systems of furnace black plants consisted of electrostatic precipitators followed by cyclone collectors. Efforts to limit the amount of carbon black escaping to the air have fostered the use of bag collectors following the conventional collecting units, and recently plants have been built in which the electrostatic precipitators have been eliminated. The cyclone collectors are still used ahead of the bag filters to reduce the load on these units.

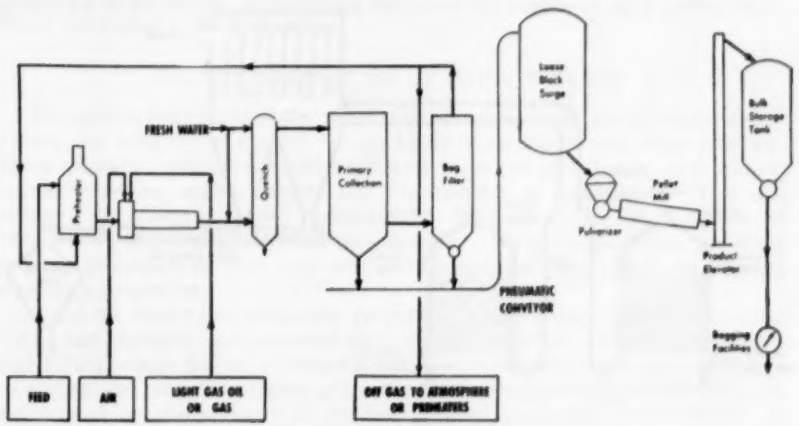


FIG. 2.—Flow sheet of process for making oil furnace black. (Courtesy of *Oil and Gas Journal*[14].)

The carbon black which emerges from the collecting system has an apparent specific gravity of roughly 0.05 equivalent to 3 lbs per cu ft. This material is conveyed first to micropulverizers which reduce any gritty material present to very fine particle size; then the carbon black is pelleted and conveyed to storage. Pelleting furnace black is much more difficult than pelleting channel black. Furthermore, the inherent property of "stickiness" of furnace black places higher demands on pellets of these blacks if they are to be suitable for bulk handling.

Basically, the combustion and pyrolysis is similar in plants using gas or oil for their raw materials. In practice, though, technical, technological and economic factors generally act to make considerable differences in the physical plants and their operation. Natural gas is comparatively difficult to pyrolize to carbon black, and much of the raw material is consumed to produce heat. On the other hand, the oils commonly used for carbon black manufacture have been degraded in refining so they can readily be cracked to produce carbon

black. As a consequence, grain loadings (concentration) of the carbon black in the gas stream from furnaces designed to operate on oil are considerably higher than is common in gas-fired operations. This alters the sizes of the furnaces, collecting and pelleting units relative to each other. Furthermore, the basic properties of the carbon blacks are sufficiently different to alter the sizes and to some extent the nature of the pelleting, handling and storage systems.

For a good description of the equipment used in constructing an oil furnace black plant, see the paper by Shearon, Reinke and Ruble[15].

3. The thermal process (cf. Figure 3).—The thermal process is a cyclic operation[16]. The carbon black is formed in large converters filled with a refractory brick checkerwork. Two converters are operated together, one on the heating cycle and the other on the reaction or make cycle. On the heating cycle, natural gas is burned to preheat the brick checkerwork; the temperature is reported to

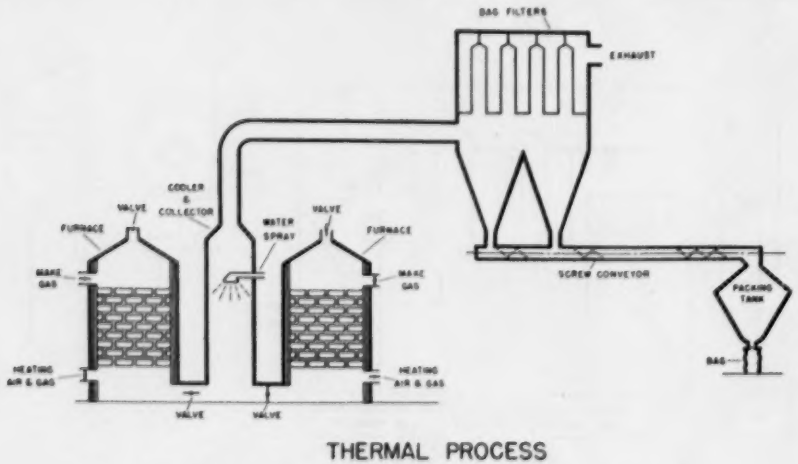


FIG. 3.—Flow sheet of process for making thermal black. (Courtesy of Interscience Encyclopedia, Inc., New York[19].)

attain a maximum of about 2600° F. On the make cycle, the air is shut off, and the natural gas is cracked mainly to carbon and hydrogen by the hot refractory. The units are reported to be on heating cycle for 5 minutes and on make cycle for an equal length of time. The process as described so far would make a black of large particle size, medium thermal black. A fine thermal black is made in the same manner except that the hydrogen off-gas is recycled with natural gas on the make cycle. Fine thermal black is the only rubber-grade carbon black made in the USA which contains very much extractable matter (tarry material which can be extracted from the carbon with organic solvents like benzene, acetone, etc.). Values in the order of 1% or more extractable in 22 hours by benzene are usual for fine thermal black.

4. The acetylene process.—Very little has been published outside the patent literature on the process by which Shawinigan acetylene black is made[17]. However, a reasonable amount of information is contained in the patent by Kaufmann and Hall[18] which is reported[19] to cover the actual process employed.

Acetylene decomposes spontaneously and exothermally at about 800° C

forming acetylene black, hydrogen and traces of tarry materials. The cylindrical furnace has a tapered outlet section. It is heated to the decomposition temperature by combustion. Then acetylene is fed into the furnace and dissociation into acetylene black and hydrogen takes place. As the hydrogen which contains the product emerges from the furnace, it is ignited and the carbon black conveyed to packing and densifying facilities. This type of carbon is not pelleted but instead is compressed to approximately 6.25 lbs per cu ft (50% compression) or to 12.5 lbs per cu ft (100% compression).

Having discussed the processes by which rubber-grade carbon blacks are manufactured, we are now in position to discuss the various types more specifically. What makes a channel black different from a furnace black or a thermal black? What is different about two types of furnace blacks? To become more specific, we must discuss properties of the various types of carbon black listed in Table I, the materials being identified by their trademarks. Here, one is faced with the problem of just which of the multitude of properties which we can measure in the laboratory should be considered in attempting to set out the distinguishing features of the various types of carbon black. This is the subject of the next section.

III. THE PROPERTIES OF CARBON BLACK

The author believes that five properties of carbon black are critical in determining the behavior of a given carbon black in rubber or any other medium. These primary (perhaps fundamental) properties are *particle size*, *surface area*, *hydrogen content*, *ozygen content* and the *tendency to agglomerate*. This last property is generally called "structure". With the possible exception of "structure", they can all be measured directly. We shall discuss each of these primary properties in turn, and only briefly mention their effects on selected secondary properties.

What we refer to as secondary properties include: color index, nigrometer value, tint strength, iodine adsorption, DPG adsorption, volatile, pH, roughness factor, shape factor, unsaturation factor, wettability, charge, resistivity, oil absorption, etc. The values of these secondary properties are believed to be determined by one or more of the five primary properties listed above. It would be inappropriate to discuss these secondary properties at length in this paper, but brief mention will be made to some which can be directly related to one or more of the primary properties or which are of importance to rubber compounders.

It would be difficult to discuss these properties without using examples, and the data in Tables II, III, IV, V, VI, and VII are presented to give a comprehensive set of properties for a group of samples which represent each type of rubber-grade carbon black produced in the United States and one German black, CK-4, which is commonly used in Europe. Whenever possible in this paper, data obtained using these particular samples of carbon black will be employed in our illustrations.

The effect of impurities in the carbon black[20], including ash, moisture, occluded gases, extractable matter and grit, in the amounts normally present, are generally considered to be negligible in determining the behavior of a given carbon black in rubber or other media. Occasional exceptions to this statement are found when the quantity of these impurities becomes excessive or when the use is of a very special nature. For example, extremely low grit content may be required for a rubber thread application, or low ash may be needed in a metallurgical application where the carbon is used as a reducing agent in making a very pure metal. It should be pointed out that moisture affects rate of cure

with many curing systems, no matter how it be introduced into the compound, and the compounder should take this into account. Judged by the quantities of such impurities, carbon black ranks with the purest compounding ingredients which are used in rubber.

A. PARTICLE SIZE

Particle size measurements on carbon black are now almost universally made using the electron microscope, and these are generally considered to be the

TABLE II

AVERAGE PARTICLE SIZE, SURFACE AREA AND ULTIMATE COMPOSITION OF VARIOUS CARBON BLACKS

Trade-mark	Condition[1]	Type[2]	Av. E.M. Particle Diameter	BET surface area (N_2 Adsorption)	% Drying loss	%H[3]	% C	% Ash	% S	% O by Difference
Rubber-Grade Blacks										
Thermax	U	MT	2900 A	8.2 m²/g	0.04	0.36 (0.33)	99.42	0.27	0.01	[−0.06][4]
P-33	U	FT	1485	16.3	0.09	0.49 (0.47)	99.31	0.09	0.01	0.10
Pelletex	P	SRF	648	27.1	0.00	0.39 (0.38)	99.18	0.21	0.00	0.22
Sterling V	P	GPF	557	29.2	0.03	0.37 (0.36)	98.64	0.23	0.55	0.21
Kosmos 40	P	HMF	525	31.2	0.00	0.36 (0.35)	98.75	0.39	0.23	0.23
Shawinigan	U	ACET.	408	66.8	0.03	0.08 (0.09)	99.75	0.00	0.02	0.15
Statex B	P	FF	560	48.3	0.15	0.39 (0.36)	98.22	0.95	0.01	0.43
Philblack A	P	FEF	384	45.8	0.16	0.38 (0.35)	98.41	0.16	0.67	0.58
Philblack O	P	HAF	294	79.6	0.72	0.34 (0.30)	97.96	0.32	0.59	0.79
Philblack I	P	ISAF	286	116.8	0.97	0.32 (0.29)	97.56	0.44	0.51	1.17[5]
Philblack E	P	SAF	175	135.1	0.57	0.33 (0.31)	97.55	0.47	0.64	1.01[5]
Vulcan 8C	P	SCF	176	194.4	0.76	0.21 (0.17)	97.40	0.61	0.60	1.18
Spheron 9	P	EPC	320	115.8	1.32	0.66 (0.62)	95.64	0.02	0.19	3.49
Spheron 6	P	MPC	246	120.0	1.40	0.60 (0.55)	96.21	0.04	0.05	3.10
Spheron 4	P	HPC	242	152.7	1.30	0.52 (0.47)	96.16	0.04	0.00	3.28
Spheron C	P	CC	274	253.7	2.26	0.45 (0.33)	96.39	0.01	0.01	3.14
CK-4	P	German	318	83.1	1.90	0.91 (0.86)	95.62	0.03	0.51	2.93
Color Blacks										
Elf O	U	LCC	360	171.0	2.01	0.52 (0.47)	94.48	0.01	0.10	4.89
Mogul A	U	LFC	352	228.4	5.66	0.60(0.51)	91.63	0.02	0.12	7.63
Mogul	U	LFC	300	308.0	5.49	0.57 (0.48)	91.07	0.04	0.10	8.22

[1] Under condition: U—Unpelleted; P—Pelleted.

[2] Type of carbon black: MT, medium thermal; FT, fine thermal; SRF, semi-reinforcing furnace black; GPF, general purpose furnace black; HMF, high modulus furnace black; ACET., acetylene black; FF, fine furnace black; FEF, fast extrusion furnace black; HAF, high abrasion furnace black; ISAF, intermediate super abrasion furnace black; SAF, super abrasion furnace black; SCF, super conductive furnace black; EPC, easy processing channel black; MPC, medium processing channel black; HPC, hard processing furnace black; CC, conducting channel black; LCC, low color channel black; LFC, long flow channel black.

[3] Values not in parenthesis obtained by normal procedure of weighing sample between drying and combustion. Values in parenthesis obtained by special procedure in which the sample was weighed after coming to equilibrium with the laboratory atmosphere, then drying and collecting the moisture given off on drying and subtracting this moisture from the original sample weight to obtain the dry weight. These hydrogen values are believed to be superior to those obtained by the former procedure.

[4] This sample had a red (ferrous) ash which probably took up oxygen during analysis. This would *reduce* the oxygen value obtained by difference.

[5] These samples had a very strong affinity for oxygen, removing it from the containers in which they were stored and creating a vacuum. No doubt, on normal exposure to the atmosphere, their oxygen contents would increase considerably (ca. 50%) in the first month or two.

most reliable. Table II contains average particle size values for the various carbons listed. It can be seen that there is a considerable range in values from Thermax, 2900 A, to Philblack E, 175 A.

In making particle size measurements with the electron microscope, there are a number of complications which affect the results, aside from instrumental factors. When working with the high "structure" blacks, it is not easy to prepare dispersions of suitable quality for measurements. In fact, it might be questioned whether satisfactory dispersions of some of the finest furnace blacks made from oil have ever been prepared. Then there is the most important error, the human error. It would be rare, indeed, to find two people who select

the same particles for counting. This results in different final values for the average particle size (and surface areas). It is considered imperative that no particle be counted unless at least half of it be clearly visible. Then, too, it should be remembered that the size of the smallest particles of the finest carbon blacks is about equal to the resolving power of the electron microscopes, and no operator can be expected to make accurate determinations when this condition prevails. There are many who believe that, at best, isolated electron microscopic values for most reinforcing carbons (average particle sizes in the region of 250–450 A) are reliable to about 10%. In a study of the reliability of particle size determinations of carbon black by the electron microscope which was conducted by the Research Department of Phillips Petroleum Company[21], it was concluded that "with currently available techniques, electron microscope data for average particle size must differ by at least 45 A before the samples can be considered different". There seems to be a tendency when making determinations on the carbon blacks of smallest particle size to accept the lowest particle size from a series of values as the best value. Although most sources of error would be expected to lead to larger values for particle size, this practice has some obvious dangers. The author feels that difficultly dispersable carbons—the high "structure" blacks—present a special problem. When a dispersion of such a carbon black is prepared for counting, the largest particles seem to be found in the large clumps which are ignored in the counting because few clearly defined particles are present in such dense clumps. On the other hand, the electron microscopist can frequently find rather isolated clusters of very small particles which are suitable for counting. If this is true, then the particles which are counted will represent an abnormal percentage of small particles. The particle sizes so obtained will be smaller than the true value, and the surface areas larger.

For many years tests designed to determine the power of carbon black to absorb visible light have been in common use by manufacturers and consumers of carbon black. These tests, when properly run, allow the investigator to make good estimates of particle size. A very simple procedure which can be used by anyone with good eyesight to quickly differentiate between carbon blacks of different particle size consists of pouring out three piles—say 2 or 3 grams each—of the carbons in question on a flat surface, like the lid of a can, so the edges of each pile meet the edges of the other two piles like a pie cut in thirds. If the whole is viewed under a *strong light* (bright sunlight is excellent), the relative blackness determines which carbon or carbons have the smallest particle size. This test is quite useful in instances where there is doubt as to whether a sample from a storage bin is an HAF, say, or an FEF black. By comparing the unknown with known samples of HAF and FEF blacks, it is easy to determine which of the two types is in the bin. Of course, the test is best when differentiating between samples of widely different particle size.

A much more accurate test, suitable for small differences in particle size, uses the nigrometer, developed by the Godfrey L. Cabot Company. (Any sensitive instrument designed to measure small differences in reflectivity of intensely black mixtures could be used instead of the nigrometer.) Carbon black-oil mixtures are made up by mulling and transferred to a *clean* 2 inch × 3 inch glass slide. This is placed in the instrument and, after adjustment, the relative light absorption read from an inverse logarithmic scale. The author suggests that a good, white grade of mineral oil, like Nujol or Squibb's mineral oil, be used in the test rather than a polar oil, like linseed oil. This should reduce differences in agglomeration between carbon blacks of widely different

nature. Values for nigrometer value and particle size of a wide range of carbon blacks are listed in a publication of Godfrey L. Cabot, Inc.[22]. These values are plotted in Figure 4. This is analogous to a plot presented by Smith Thornhill and Bray[22]. The correlation is quite satisfactory for all but the carbons of smallest particle size made from oil. In these cases, one is tempted to believe that the nigrometer values permit more reliable estimates of particle size then the electron microscope.

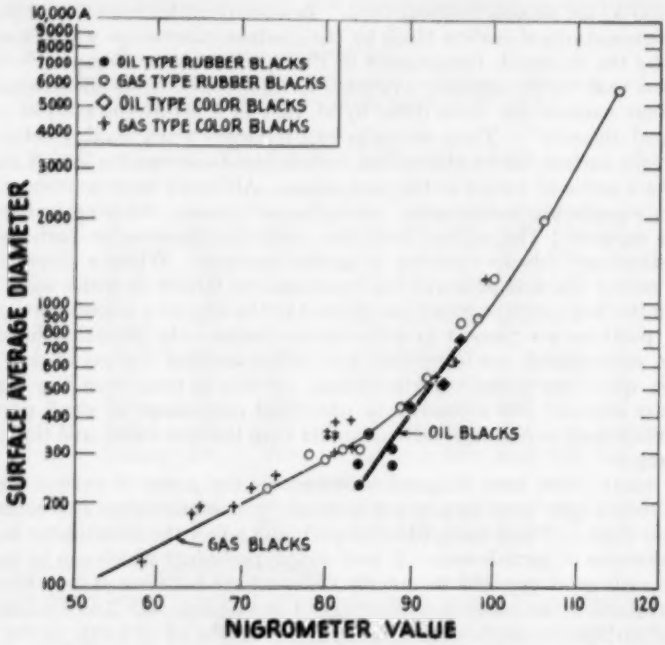


FIG. 4.—Relationship between nigrometer values and particle size measured by the electron microscope. The data are taken from Reference 22.

B. SURFACE AREA

The most reliable method of determining the surface area of a given quantity of carbon black—actually specific surface area—is generally believed to be that developed by Brunauer, Emmett and Teller (BET method) based on nitrogen adsorption[24].

The physical adsorption of vapors on a solid generally obeys a type of isotherm to which the BET equation applies over a range of relative pressures from 0.05 to 0.35 or higher. The equation in its linear form is:

$$\frac{p}{v(p_s - p)} = \frac{1}{v_m c} + \frac{(c-1)}{v_m c} \cdot \frac{p}{p_s}$$

where v is the volume of gas adsorbed, v_m is the volume of gas necessary to cover the entire surface with a unimolecular layer of adsorbed gas, p is the

equilibrium pressure, p_e is the saturation pressure of the vapor (or vapor pressure) and c is a constant at constant temperature. In practice, $\frac{p}{v(p_e - p)}$ is plotted against $\frac{p}{p_e}$, the relative pressure for the adsorbate; and, from the straight lines, values for v_m and c can be obtained.

Emmett has reviewed the method recently[25]. Applications to carbon black were described by Emmett and De Witt[26] and by Smith, Thornhill and Bray[22]. Since publication of these last two papers, the method has become accepted as a

TABLE III

MISCELLANEOUS PHYSICAL AND CHEMICAL DATA FOR VARIOUS CARBON BLACKS

Trademark	Type	Catalytic Hydrogen uptake[1]	Active Hydrogen[2]	pH[3]	Surface Area from Iodine Adsorption	Resistivity @ 734 psi
Rubber-Grade Blacks						
Thermax	MT	0.004%	0.0006%	8.24	7.6 m²/g	0.42Ω-cm
P-33	FT	0.004	0.0007	8.43	27.9	19.8
Pelletex	SRF	0.003	0.002	9.82	29.6	0.24
Sterling V	GPF	0.005	0.002	9.02	34.7	0.20
Kosmos 40	HMF	0.004	0.002	9.31	32.9	0.19
Shawinigan	ACET.	0.009	0.000	4.82	125.0	0.16
Statex B	FF	0.009	0.002	9.16	44.4	0.50
Philblack A	FEF	0.008	0.002	8.45	47.7	0.20
Philblack O	HAF	0.017	0.005	8.78	79.0	0.22
Philblack I	ISAF	0.026	0.005	8.23	116.8	0.32
Philblack E	SAF	0.026	0.004	8.41	134.9	0.40
Vulcan SC	SCF	0.025	0.007	7.22	231.6	0.22
Spheron 9	EPC	0.057	0.009	4.41	66.2	8.0
Spheron 6	MPC	0.047	0.010	4.59	62.9	5.1
Spheron 4	HPC	0.060	0.016	4.51	102.6	1.8
Spheron C	CC	0.077	0.011	5.07	165.4	0.70
CK-4	German	0.032	0.007	4.00	69.5	5.3
Color Blacks						
Elf O	LCC	0.091	0.023	3.83	105.9	3.9
Mogul A	LFC	0.085	0.024	3.05	153.1	16.4
Mogul	LFC	0.095	0.030	2.82	205.1	20.3

[1] Uptake of hydrogen at room temperature (ca. 25° C) in water with stirring in the presence of the Adams (reduced platinum oxide catalyst) during an 18-hour period.
[2] Active hydrogen determined by the Zerewitinoff method using the Grignard reagent. The sample was dried in a stream of dry nitrogen for one hour at 150° C, cooled in dry nitrogen and added to the Grignard reagent without exposure to the air.
[3] pH of slurry.

standard tool for research in the fields of carbon black and reinforcement. BET surface areas obtained from nitrogen adsorption isotherms are listed for the carbons in Table II.

The BET method is standing the test of time, and many excellent studies have been conducted to evaluate it. To the author it seems that the main point at which the procedure is vulnerable is that it assumes that, when one monolayer of nitrogen is complete, the area occupied by one nitrogen molecule is constant, independent of the nature of the adsorbent. This is very difficult to establish with absolute certainty, but the area per molecule in the monolayer may well be constant to within some 10 to 20%. If this figure is of the right order, then the absolute accuracy of the method would be limited to

about this figure. Reproducibility is much better than this; with careful work, duplicability of 1 or 2% is common.

The particle sizes and surface areas of shipments of a given type of carbon black are generally held to quite narrow limits. If a large number of samples representing various brands of a given type of carbon black are analyzed, the surface areas will generally not vary more than 10%. Day in and day out, shipments of a given brand of carbon black from a specific plant should not vary by more than 5%. In some plants the variation over a period of a year, say, is considerably less than that amount. These percentages should apply to particle size measurements as well.

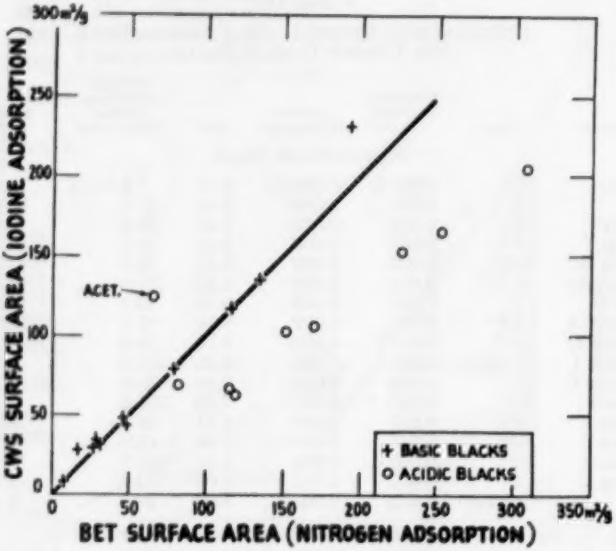


FIG. 5.—Comparison between CWS surface areas and BET surface areas. The CWS method is meant to be used on basic carbons only.

C. W. Snow[27], after analyzing an enormous amount of data on the adsorption of iodine by various carbon blacks, devised a simple procedure (referred to here as the CWS method) for determining the surface areas of basic carbon blacks which is suitable for control work at furnace black and rubber factories. The ratio of iodide ions to iodine and the concentrations of the solutions is very important. Furthermore, the surface of the sample should not be so large as to adsorb more than about 90 to 100 mg of iodine from the solution. Under the conditions specified by Snow, the adsorption of one mg of iodine corresponds to one square meter of surface. Snow's procedure is as follows.

Weigh 1.000 g of pelleted carbon black and transfer into an iodine flask. Add 5 ml of iodine solution (142.5 g potassium iodide plus 15.00 g. iodine in 250 ml water) and allow to stand untouched for 2 hours. Add 45 ml water, stopper and swirl gently for one minute; then allow to stand for one hour. Pipette 20 ml from the top of the solution and titrate with 0.0394 N sodium thiosulfate (9.781 g $Na_2S_2O_3 \cdot 5H_2O$ per liter) using a starch indicator. If all solutions are exactly of the prescribed strength, the surface area in square meters will be

equal to: $12.5 \times (24 - ml)$, where *ml* is the number of milliliters of thiosulfate required to titrate a 20 ml aliquot of the iodine solution withdrawn from the iodine flask.

To demonstrate the utility of this test, iodine adsorptions were run on the samples in Table III by the CWS method, and the areas so obtained are plotted against the BET (nitrogen adsorption) surface areas in Figure 5. The correlation is good for all definitely basic carbons. Vulcan SC is very feebly basic and shows the greatest deviation of the basic carbons. Experience with the method has shown that it is rare for the two areas to correlate well when the carbons are acidic.

C. HYDROGEN CONTENT

The two most important noncarbon constituents of carbon black are hydrogen and oxygen. Values for these are normally obtained by combustion analysis. The sample is burned in a stream of oxygen to carbon dioxide and water. These combustion products are collected in absorption tubes, weighed and calculated as carbon and hydrogen. The residue is weighed and reported as ash. Sulfur analyses are made in a separate combustion apparatus. Any sulfur in the sample is converted into sulfuric acid and determined as barium or silver sulfate. Oxygen contents are then calculated by difference. There are many variations of these techniques and also other procedures possible. Because of its high carbon content, analyses for the other elements present must be of high accuracy to be useful to the carbon black chemist.

All commercial carbon blacks contain hydrogen. This hydrogen is introduced as a component in the hydrocarbon raw materials; and, when these hydrocarbons are converted to carbon black, in the flame, the conversion is not to a pure elemental carbon, like diamond or graphite, but to a material which contains some 92 to 99 *atom per cent carbon* and some 8 to 0.8 *atom per cent hydrogen* (Table VI).

To the extent that carbon black is perfectly oriented into graphitic planes, (cf. Section IV, B) each carbon atom is associated with one mobile, conducting or π electron. Combination of crystallite edge atoms with hydrogen or other "foreign" atoms would involve the localizing of these mobile electrons, and the conductivity of the carbon black would be expected to decrease. Accordingly, we might expect a relationship between hydrogen content and resistivity of dry carbon black. Data conforming to this concept have been published[28]. Actually, this relationship represents quite an oversimplification. It does not take into account the other atoms present which would also tie up mobile electrons, although hydrogen is normally by far the most abundant noncarbon element. Nor does it take into account the nonoriented or "random" carbon, the effect of impurities, the effect of pressure, densification, etc. Figure 6 shows the relationship between the resistivities of the dry carbon black samples of Table III at a pressure of 734 psi and their *atom per cent carbon* (Table VI).

The hydrogen content of carbon black is of importance in determining many other properties of the solid carbon black such as wettability[29], and its importance in determining the reactivity of carbon black will be pointed out in succeeding Section IV, D, 2 and elsewhere in this paper.

The hydrogen contents of the channel blacks tend to be higher than the hydrogen contents of furnace blacks. When rubber compounds with high conductivity are desired, carbon blacks with low hydrogen contents should be used[30]. Carbon black loading is also important[31]. At low loadings of a given

type of carbon black, the resistivity usually increases somewhat with loading. Then, as the amount of carbon black in the stock is increased further, the tendency of carbon black to agglomerate—"structure"—becomes the dominant property which determines the resistivity. At still higher loadings, the intrinsic resistivity of the carbon black becomes of greatest importance.

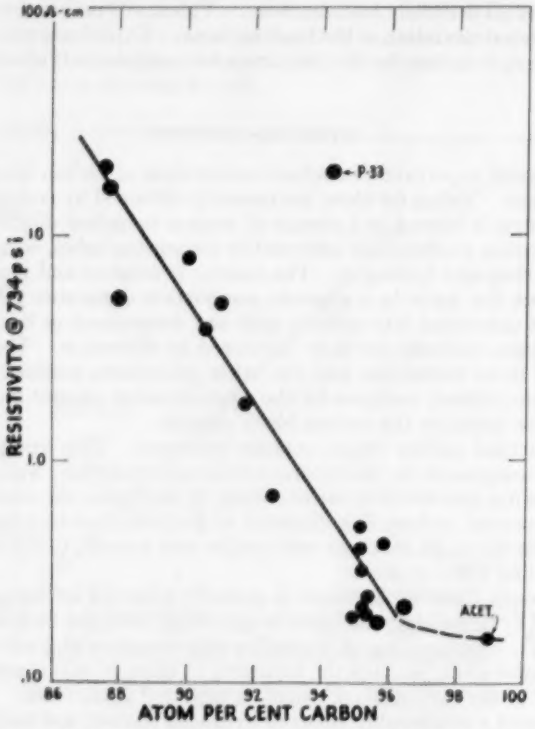


FIG. 6.—Relationship between resistivity of dry carbon black under pressure and atom per cent carbon.

D. OXYGEN CONTENT

All commercially available carbon blacks contain oxygen. So far as we know, all of the oxygen is chemically combined at the carbon black surface. (In this discussion we refer to the oxygen content as that which is determined, usually by difference, from combustion analysis, after drying at 150° C for one hour in a stream of dry, inert gas such as nitrogen, helium, etc. Hence, physically adsorbed gases like oxygen, moisture, carbon dioxide, etc. are ignored.) The surface oxygen arises from the exposure to the air and moisture of the atmosphere after the carbon black particle is formed. Autoxidation of carbon black takes place during the treatment which the sample receives in the conveying, pulverizing, pelleting, drying (if wet pelleted) equipment or in storage. This is of considerable importance in determining the oxygen content of furnace blacks. Channel blacks are exposed to air at elevated temperatures, in the

order of 1100° F, after they are deposited on the channel irons. This brief, but effective, high temperature treatment "saturates" the surface with combined oxygen.

Under the influence of the types of exposure mentioned here, the maximum amount of oxygen which a sample will contain is determined by its surface area and its hydrogen content. Thus, if oxygen content per unit of surface be plotted against hydrogen content, a graph like Figure 7 is obtained. A similar plot constructed from 32 analyses was published previously[28]. Within experimental error, data for all rubber grade channel blacks, except some samples of conducting channel black, fall on or near the line. Some conducting channel blacks fall below the line, in the region occupied by dry pelleted furnace blacks.

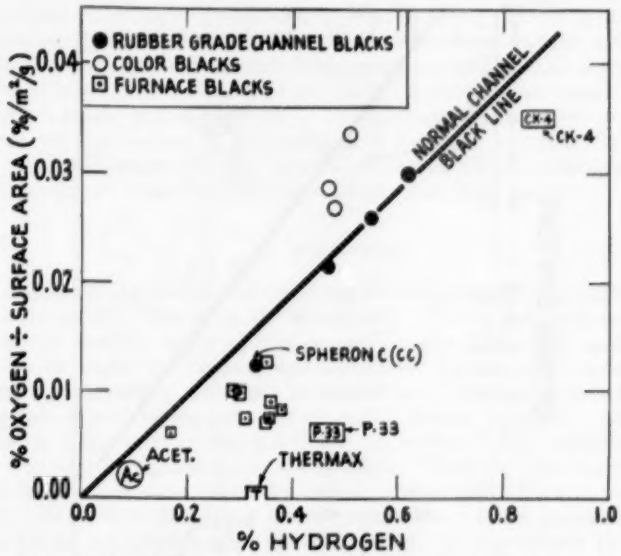


FIG. 7.—Chart showing relationship between oxygen content per unit of surface and hydrogen content of commercial carbon blacks. Data of Table II.

Such products can be produced by forming the conducting channel black in hotter flames and keeping the channel temperatures high or by after treating regular channel black at elevated temperatures.

Furnace blacks, as mentioned previously, contain but small amounts of oxygen when first removed from the furnaces. However, the oxygen content is increased during normal processing and storage. If dry pelleting is used, most of the oxygen pickup takes place in this operation. The temperature in the pellet mills varies principally with pellet mill diameter, bed depth and speed of rotation. In some cases it may be as high as 300 to 350° F, but is usually lower. Wet pelleting must be followed by drying, and in the dryers the carbon black is exposed to air at temperatures of several hundred degrees Fahrenheit. Wet process pelleted furnace blacks frequently contain the maximum amount of oxygen with which they will combine according to the line in Figure 7.

Special treatment, as with oxidizing agents in solution, or even prolonged after treatment at temperatures in the nieghborhood of 400° C, will add more

oxygen than is indicated on the channel black line, Figure 7. Special grades of ink and color blacks are examples of such products (Elf O, Mogul A and Mogul) on the figure. If one recognizes this limitation, Figure 7 represents a very useful relationship. It seems to represent what can be expected of rubber grade blacks as normally produced.

For many years the pH of aqueous carbon black slurries has been used to evaluate the "acidity" of the carbon blacks[32]. Slurries of the high oxygen color blacks are quite acidic; the rubber grade channel blacks are somewhat less acidic; and the furnace blacks are generally definitely basic. A rather general relationship exists between the total oxygen content of the various carbon blacks and the pH of their slurries as exemplified by Figure 8 (cf. also Reference

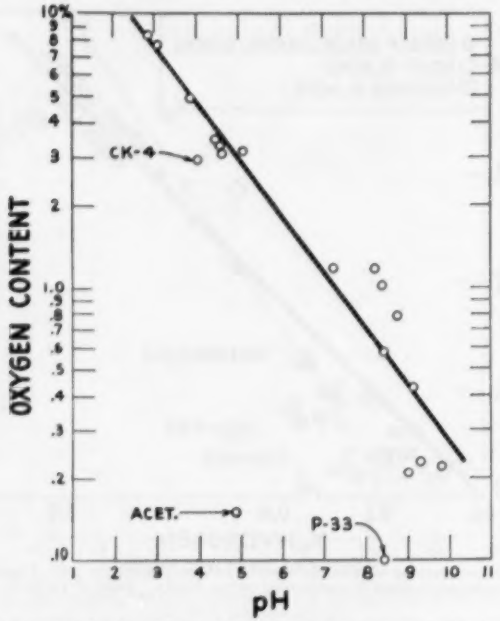


FIG. 8.—Graph showing the dependence of pH of various carbon blacks upon their oxygen contents. Data of Tables II and III.

20). The chief exceptions are Shawinigan acetylene black, which is acidic in spite of its low oxygen content, and fine thermal blacks, which are less basic than the furnace blacks of comparable oxygen content. A rough relationship like this would not be expected to be very quantitative for low oxygen blacks, particularly when the basic nature of the ash can contribute to the basicity. This alkaline ash is found only with carbons made by thermal or furnace processes; its source is the cooling water used to stop the reactions and to adjust the temperature of the gas stream so it can be handled by the collecting system. It is a common fallacy that the basic nature of furnace blacks is due to this alkaline ash. This can be refuted by the following experimental evidence:

(1) Channel blacks contain no alkaline ash. When they are heat treated in an inert atmosphere to reduce or completely remove their oxygen content, they are definitely basic[32].

(2) When a furnace black (Philblack O) was made using distilled water for quenching, the product was basic, exhibiting but slight change in pH from samples made with the normal quench water which contained alkaline salts[33]. The pH of the freshly prepared Philblack O was above 9 whether normal quench water or distilled water was used.

(3) A sample of the FEF black, Philblack A, was prepared by taking the sample at the outlet of the reactor but without quenching the gas stream. Its pH was 10.5. Another sample taken from the same reactor, operated under identical conditions except with normal quench water, had a pH of 9.5[34].

What, then, is the reason for the basic character of most low-oxygen carbon blacks? It is suggested that it is related to the resemblance of these carbons to polycondensed aromatic hydrocarbons which are known to be Lewis bases (electron donors) (cf. Section IV, A). Such materials might reasonably be expected to preferentially adsorb hydrogen ions rather than hydroxyl ions. This would leave the surrounding liquid in the slurry with an excess of hydroxyl ions, which would give a basic pH. To the extent that oxygen is chemically combined at the surface, it will counteract the basic character in the Lewis sense. This will be true for any oxygen-containing groups, although the actual acidity developed would be quite dependent upon their nature.

E. "STRUCTURE"

Undoubtedly the most nebulous of the primary properties of carbon black is the one commonly referred to as "structure". To the author it seems that a more precise term to apply to this property is the *tendency to agglomerate*, or perhaps even better the *forces of agglomeration*. Carbon black exhibits a pronounced agglomerating tendency in almost any medium. Dispersions containing only monodisperse particles are rarely, if ever, attained. As soon as it emerges from the flame in which it is formed, carbon black exists as agglomerates. Consider its apparent specific gravity. When the true specific gravity of carbon black is determined by helium displacement[35], it is found to be 1.8–2.1. Yet, the carbon black which emerges from a hot house or collecting system has an apparent specific gravity of 0.05. If a container be filled with such fluffy carbon black, it will contain 2.5% carbon particles by volume and 97.5% occluded air or gas. It is difficult to visualize the looseness of such a packing. Attempting to construct a mechanical model which contains this high ratio of voids to solids, using marbles to represent the carbon black particles, is quite instructive.

This tendency to agglomerate is believed to be due to the operation of long-range London-van der Waals forces, e.g., dispersion forces, which operate between the carbon black particles[36]. If such forces did not exist, we would be unable to form stable pellets of dry carbon black. The stickiness of carbon black as if flows down a chute is familiar to rubber technologists. Although in some instances moisture can aggravate this stickiness, it is not necessary because extremely dry carbon black exhibits this property.

Particle size influences every simple test by which we attempt to evaluate this tendency to agglomerate. This is unfortunate in a way, for it makes it almost impossible to designate the relative tendency to agglomerate by unequivocal numerical values. Sweitzer and Goodrich[37] attempted to assign such values, which they refer to as a "structure index", using oil absorption and particle size measurements; but, until the effect of particle size can definitely

be established, these values can only be used with any degree of confidence in comparing carbons of similar particle size and comparable densification[28].

The following statements probably can be made without inciting argument:

(1) Acetylene black displays "structure" properties as high as or higher than any other commercially available carbon black. The super-conducting furnace black, Vulcan SC, also has extremely high agglomerating properties.

(2) The oil furnace blacks have a higher "structure" than the furnace blacks made from gas.

(3) The channel blacks, with the possible exception of the conducting channels, possess less "structure" than most furnace blacks made from gas. The agglomerating properties appear to decrease in the order CC, HPC, MPC, EPC. It seems likely that the conducting channels should be considered to possess agglomerating properties almost as pronounced as the oil furnace blacks; the easy processing channel blacks may be more nearly comparable to thermal blacks in this property.

(4) Thermal blacks, at least the fine thermal blacks, have the lowest structure.

(5) Fine furnace black is considered to have a lower structure than other furnace blacks made from gas.

A tentative grouping of carbon blacks in order of their agglomerating tendencies then would be:

(1) Acetylene black and super conducting furnace blacks, highest.
(2) Most oil furnace blacks.
(3) Gas furnace blacks.
(4) Medium and easy processing channel blacks.
(5) Thermal blacks, at least FT, lowest.

The placement of CC, HPC, MT, FF and GPF blacks might be subject to some question.

The tendency to agglomerate seems to be dependent in some way on the ultimate structure (cf. Section IV, B) of the carbon black. This concept was arrived at empirically but may have some theoretical justification.

If we think of the carbon atoms in a carbon black particle as being chemically like carbon atoms in normal condensed polycyclic aromatic compounds, then virtually all of the valency requirements of each carbon atom are fully satisfied except at the edges of the crystallites. There, insufficient hydrogen, oxygen, etc. atoms are available to satisfy all the valency requirements and unpaired electrons would be expected. If, as an approximation, we calculate the number of edge atoms of the crystallite and compare it with the number of hydrogen atoms, we can obtain a rough measure of the unsatisfied valences. We can express this as a ratio of edge carbon atoms to hydrogen atoms, or we can present the data graphically as in Figure 9. The fraction of the carbon atoms which are at the edges of the layer planes is equal to $\frac{4}{L_a}$.

It is observed that the carbons which show an abnormally high tendency to agglomerate—high "structure"—fall on the side of the line representing the smallest amount of hydrogen in the sample per crystallite edge atom. The low "structure" blacks fall on the opposite side of the graph. In fact, it is possible to obtain a reasonably satisfactory separation of the rubber grade carbon blacks into areas representing various degrees of "structure". This, then, points to a relationship between the ultimate structure of carbon black as revealed by x-ray

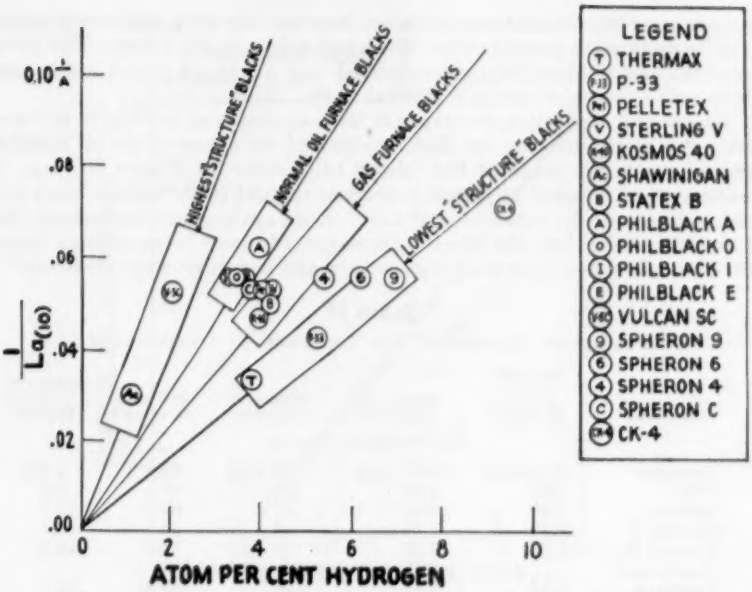


FIG. 9.—Structure chart for rubber-grade carbon blacks. Data of Tables V and VI.

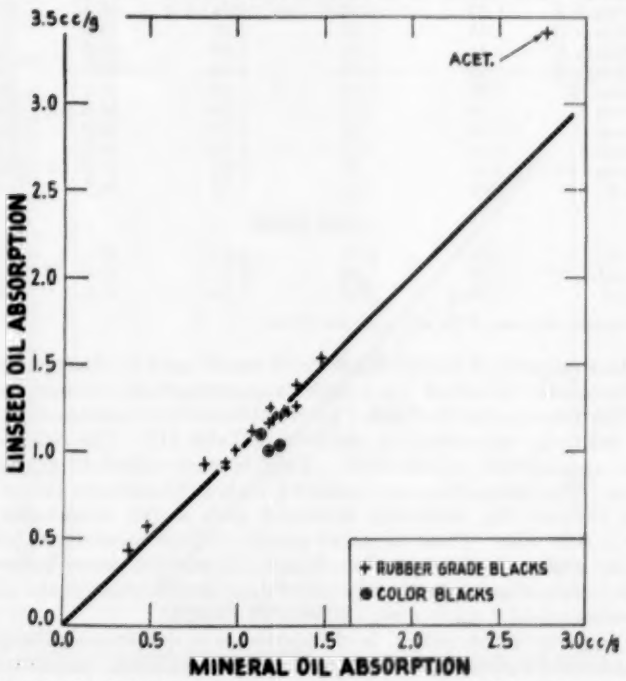


FIG. 10.—Graph showing that the oil absorption values are almost independent of the nature of the oil at the single ball stage. Data of Table IV.

analysis and ultimate analyses on the one hand and the property loosely referred to as "structure" in general carbon black technology on the other. The picture presented here is admittedly oversimplified, and it is hoped that it will be possible to refine this relationship somewhat in the future.

Because oil absorption is commonly used to obtain an indication of "structure", it is worth pointing out that the effect of the nature of the oil is slight if the end points are taken at the "single ball" state (cf. Figure 10), e.g., the quantity of oil required to permit a weighed amount of the carbon black to be worked into a single, coherent, stiff ball. Data are available to indicate that, at the other end points, the effect of the nature of the oil becomes more important, especially when comparing high-oxygen and low-oxygen carbon blacks[39].

TABLE IV

PROPERTIES RELATED TO THE TENDENCY TO AGGLOMERATE

Trademark	Apparent specific volume @ 734 psi	Linseed oil absorption	Mineral oil absorption	Extrusion shrinkage*	Decrease in % extrusion shrinkage
		Rubber-Grade Blacks			
Thermax	0.85 cc/g	0.43 cc/g	.38 cc/g	68.5%	4.4%
P-33	1.05	0.57	.48	67.1	5.8
Pelletex	1.23	0.93	.81	62.2	10.7
Sterling V	1.35	1.01	.99	54.5	18.4
Kosmos 40	1.27	0.92	.93	57.0	15.9
Shawinigan Acetylene	2.16	3.41	2.78	37.6	35.3
Statex B	1.31	0.94	.93	61.4	11.5
Philblack A	1.50	1.26	1.34	45.4	27.5
Philblack O	1.48	1.24	1.27	49.6	23.3
Philblack I	1.54	1.24	1.27	51.3	21.6
Philblack E	1.63	1.39	1.34	53.7	19.2
Vulcan SC	1.71	1.54	1.48	47.1	25.8
Speron 9	1.55	1.18	1.20	58.8	14.1
Speron 6	1.55	1.25	1.19	59.9	13.0
Speron 4	1.54	1.17	1.18	60.2	12.7
Speron C	1.51	1.20	1.25	57.4	15.5
CK-4	1.64	1.12	1.08	58.5	14.4
		Color Blacks			
Elf O	1.71	1.10	1.14	59.1	13.8
Mogul A	1.74	1.00	1.18	60.4	12.5
Mogul	1.79	1.03	1.24	59.8	13.1

* The extrusion shrinkage of the gum stock was 72.9%.

Another property of carbon black which can be used to obtain an indication of the "structure" of carbon black is the apparent specific volume under pressure. The data reported in Table IV were obtained in the same cell as was used for the resistivity measurements reported in Table III. The cell had a cross sectional area of 0.11 square inch. Weights were added to attain various pressures. The resistivities are measured with a Wheatstone bridge and the distance between the electrodes measured with a dial micrometer reading directly in 0.01 mm. These apparent specific volume measurements correlate reasonably well with oil absorption, Figure 11, possibly being preferable because they are not as markedly dependent upon densification as the oil absorption measurements.

The property of "structure" is of importance in determining the properties of unvulcanized rubber mixtures containing carbon black, particularly those

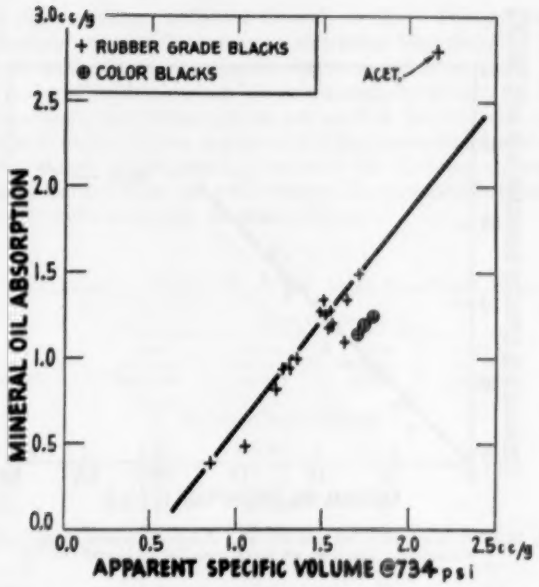


FIG. 11.—The relationship between oil absorption and specific volume of dry carbon black under pressure.

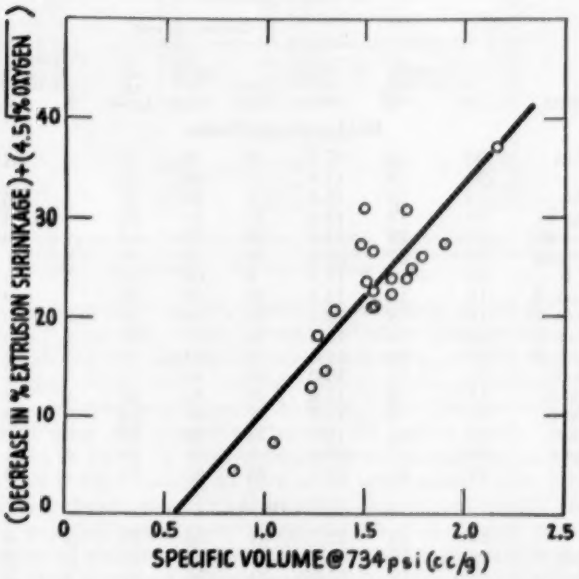


FIG. 12.—The relationship between extrusion shrinkage, oxygen content and specific volume under pressure. The data are taken from Tables II and IV.

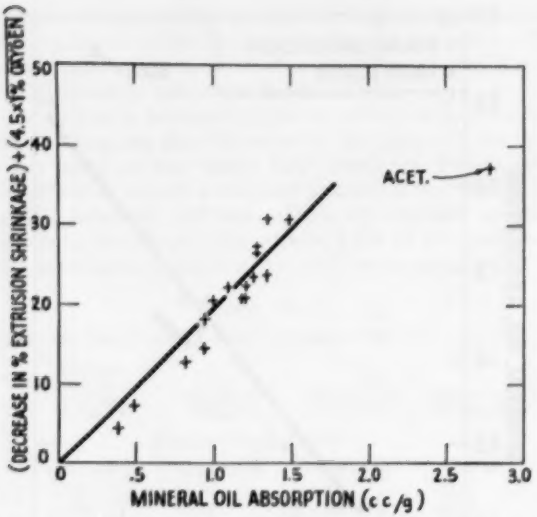


FIG. 13.—The relationship between extrusion shrinkage, oxygen content and oil absorption. The data are taken from Tables II and IV.

TABLE V

X-RAY ANALYSES

Trademark	Crystallite dimensions, A: L_a (breadth) (10)	L_a (breadth) (11)	L_c (height) (002)	Carbon per cent: Random	In parallel layers	In single layers	Probability of number of parallel layers: 3	4	5
Rubber-Grade Blacks									
Thermax	30	20	17.3	9	78	13		.1	.9
P-33	23	18	17.6	13	62	25			1.0
Pelletex	19	14	15.5	9	68	23		.6	.4
Sterling V	19	14	14.8	13	64	23		.8	.2
Kosmos 40	21	18	14.8	10	72	18		.8	.2
Shawinigan	30	27	24.6	11	78	11	*		
Statex B	20	16	13.7	6	69	25	.1	.9	
Philblack A	16	15	14.4	18	60	22		.9	.1
Philblack O	18	18	12.7	23	58	19	.4	.6	
Philblack I	18	18	12.3	23	54	23	.5	.5	
Philblack E	18	18	11.6	19	64	17	.7	.3	
Vulcan SC	19	15	13.0	21	45	34	.3	.7	
Spheron 9	18	14	13.4	16	52	32	.2	.8	
Spheron 6	18	12	13.7	17	61	22	.1	.9	
Spheron 4	18	13	12.7	13	60	27	.4	.6	
Spheron C	19	17	12.0	9	67	24	.6	.4	
CK-4	14	11	12.7	26	55	19	.4	.6	
Color Blacks									
Elf O	15	15	12.7	31	36	33	.4	.6	
Mogul A	16	14	14.4	17	52	31		.9	.1
Mogul	15.5	12	13.0	31	37	32	.3	.7	

* Approx. mean number of layers equals 7.

determining the processing behavior of such stocks. The influence of "structure" on Mooney viscosity[38] and upon extrusion shrinkage[20,40] has been discussed. Reasonably good correlation between oil absorption and Mooney viscosity of natural rubber-carbon black masterbatches can be demonstrated, providing reasonably low temperatures are used in the mixing. As the mixing temperature is increased, there is apparently an interaction between the rubber and the carbon black which generally reduces the Mooney viscosity. But the effect of mixing temperature upon the carbon black masterbatches is somewhat different for the different types of carbon black[41].

TABLE VI

ANALYSES OF TABLE II ON AN ATOM PER CENT BASIS

Trademark	First analyses: Atom per cent hydrogen	Atom per cent carbon	Atom per cent sulfur	Atom per cent oxygen	"Best" value* atom per cent hydrogen
Rubber-Grade Blacks					
Thermax	4.1	95.86	0.03	0.00	3.8
P-33	5.6	94.38	.003	.07	5.3
Pelletex	4.5	95.37	.00	.16	4.0
Sterling V	4.3	95.38	.20	.15	4.2
Kosmos 40	4.2	95.60	.08	.17	4.0
Shawinigan	0.9$_5$	98.93	.007	.11	1.0$_6$
Statex B	4.5	95.18	.003	.31	4.2
Philblack A	4.4	94.97	.24	.42	4.0
Philblack O	3.9	95.27	.21	.58	3.5
Philblack I	3.7	95.23	.19	.86	3.4
Philblack E	3.8	95.19	.23	.74	3.6
Vulcan SC	2.5	96.42	.22	.88	2.0
Spheron 9	7.4	90.06	.07	2.47	7.0
Spheron 6	6.8	91.01	.02	2.20	6.2
Spheron 4	5.9	91.74	.00	2.35	5.4
Spheron C	5.2	92.58	.003	2.26	3.8
CK-4	10.0	87.84	.18	2.02	9.5
Color Blacks					
Elf O	5.9	90.51	.04	3.52	5.4
Mogul A	6.8	87.64	.04	5.48	5.9
Mogul	6.5	87.51	.04	5.93	5.6

* These hydrogen values were obtained at a later analysis. The analysis was improved by drying in nitrogen and burning without exposure to the air. Heretofore, we have been drying—weighing to get dry weight—then returning to the combustion tube for combustion.

The same general statements apply to extrusion shrinkage of SBR and butyl rubber. When the mixing is conducted at low temperatures, the correlation with oil absorption is generally reasonably good, but the correlation is not good for higher temperature mixing. Here, again, a carbon black-rubber interaction appears to be involved. At least part of the interaction appears to be dependent upon the oxygen content of the carbon black. The extrusion shrinkage data in Table IV were obtained on samples mixed at approximately 250° F, which is high enough to give some interaction. The correlation between extrusion shrinkage and oil absorption, or apparent specific volume under pressure, is not very satisfactory unless the effect of oxygen content is introduced, Figures 12 and 13. This carbon black-rubber interaction appears to be the same as that described in butyl-carbon black mixes by Gessler[42–45] and in natural and butyl masterbatches by Barton, Smallwood and Ganzhorn[46].

TABLE VII

RUBBER PROPERTIES OF THE VARIOUS CARBON BLACKS IN HOT SBR RUBBER *

		Rubber blacks										
Trademark		Thermax	P-33	Pelletex	Sterling V	Kosmos 40	Shawinigan	Statex B	Phil-black A	Phil-black O	Phil-black I	Phil-black E
Type		MT	FT	SRF	GPF	HMF	ACET	FF	FEF	HAF	ISAF	SAF
	Cure @ 307° F											
Mooney viscosity (ML-4′ @ 212° F)	—	37	40	44	50	48	63	49	55	57	65	74
Mooney scorch (min @ 280° F)	—	36	36	29	29	29	31	26	26	21	20	17
300% Moduls (psi)	15′	210	225	590	900	860	1000	650	1180	1480	1325	1240
	30′	410	430	1150	1520	1400	1840	1200	2000	2160	2150	2000
	45′	400	400	1160	1560	1400	1850	1275	2040	2350	2225	2100
	60′	400	410	1140	1650	1425	1825	1340	1975	2240	2320	2190
Tensile strength (psi)	15′	840	1710	1825	2150	2150	1850	2440	2160	2775	3080	3110
	30′	990	1560	2025	2390	2225	2340	2610	2720	3375	3780	3725
	45′	840	1575	2225	2460	2060	2300	2900	2640	3250	3480	3725
	60′	910	1625	2225	2550	2175	2300	2710	2460	3360	3590	3700
% Elongation @ break	15′	1020	990	720	650	635	575	705	520	515	520	555
	30′	565	665	490	470	455	410	505	410	425	465	455
	45′	500	670	510	455	420	390	525	390	400	405	435
	60′	540	650	540	465	445	410	530	375	400	410	415
Shore A hardness	15′	39	44	50	56	53	57	55	58	63	64	67
	30′	48	50	57	60	58	65	59	63	67	67	70
	45′	48	51	57	60	59	66	59	64	67	69	70
	60′	48	51	57	60	59	66	60	65	67	70	70

TABLE VII—(*Continued*)

		Rubber blacks										
Trademark		Thermax	P-33	Pelletex	Sterling V	Kosmos 40	Shawinigan	Statex B	Phillblack A	Phillblack O	Phillblack I	Phillblack E
Type		MT	FT	SRF	GPF	HMF	ACET	FF	FEF	HAF	ISAF	SAF
	Cure @ 307° F											
Heat buildup (°F)	45′	46	44	53	53	51	61	56	57	63	65	67
Yerzley resilience (%)	45′	62.0	65.3	59.8	62.0	61.7	56.9	56.2	58.8	63.3	51.5	48.5
% Compression set (ASTM-B)	30′	29.4	25.9	26.2	22.7	24.7	25.8	27.6	24.6	26.3	27.5	34.3
	45′	20.3	20.5	20.0	18.5	18.5	18.7	20.3	17.1	20.4	21.8	23.7
Crescent tear @ 212° F	15′	46	95	173	194	205	133	216	144	232	246	259
	30′	42	67	94	87	96	105	159	99	160	170	230
	45′	31	61	68	103	68	106	156	86	164	207	194
	65′	42	42	81	81	57	77	148	92	145	175	198
Goodyear angle abrasion (cc. loss—1200 Rev.)	45′	32.3**	24.6**	11.3	10.2	18.2	9.4	8.4	7.0	4.0	3.0	3.1
Specific gravity	60′	1.148	1.143	1.150	1.141	1.145	1.148	1.148	1.141	1.142	1.138	1.137

* Compound: Philprene ® 1000, 100.0; carbon black, 50.0; zinc oxide, 5.00; stearic acid, 2.00; BLE Powder, 1.25; Paraflux, 2.00; Circosol 2-XH, 2.00; Sulfur, 1.80; Santocure, 1.00. Banbury temperature was held as close to 250° F as possible by adjusting cooling water and steam. For extrusion shrinkage results for these stocks, see Table IV. ® is a registered trademark.

** These samples could only be run for 600 revolutions. The loss at 600 revolutions was multiplied by 2 to obtain the values in the table.

TABLE VII—(*Continued*)

		Rubber blacks						Color blacks			Gum stock
Trademark		Vulcan SC	Spheron 9	Spheron 6	Spheron 4	Spheron C	CK-4	ELF O	Mogul A	Mogul	
Type		CF	EPC	MPC	HPC	CC	German	LCC	LFC	LFC	No black
	Cure @ 307° F										
Mooney viscosity (ML-4′ @ 212° F)	—	67	60	62	65	76	59	66	64	68	28
Mooney scorch (min @ 280° F)	—	32	30	27	25	26	25	25	28	29	43
300% Modulus (psi)	15′	550	725	720	850	580	1010	960	960	520	—
	30′	1610	1700	1500	1425	1080	1800	1580	1560	1180	190
	45′	1825	1850	1640	1525	1190	1975	1775	1760	1400	160
	60′	1890	1950	1820	1540	1310	2050	1840	1875	1560	170
Tensile strength (psi)	15′	1660	2650	2720	3320	2960	2750	3300	3150	2220	—
	30′	3375	2820	3480	3550	4240	3110	3220	3160	3190	210
	45′	3480	2780	3240	3375	4080	3420	3260	3040	3040	210
	60′	3300	2750	3025	3625	4200	3140	3090	3100	3240	210
% Elongation @ break	15′	660	715	680	680	750	640	630	655	765	—
	30′	515	455	520	545	630	460	460	465	575	375
	45′	460	405	475	485	595	450	445	445	510	365
	60′	450	380	425	510	575	405	415	425	515	350

TABLE VII—(*Continued*)

		Rubber blacks						Color blacks			Gum stock
Trademark		Vulcan SC	Spheron 9	Spheron 6	Spheron 4	Spheron C	CK-4	ELF O	Mogul A	Mogul	
Type		CF	EPC	MPC	HPC	CC	German	LCC	LFC	LFC	No black
	Cure @ 307° F										
Shore A hardness	15′	60	59	61	63	64	62	65	62	60	26
	30′	66	67	67	67	68	66	70	67	67	38
	45′	67	67	67	68	70	67	70	68	68	39
	60′	68	67	67	68	70	68	70	68	68	39
Heat buildup (° F)	45′	67	57	58	63	69	58	59	58	67	Too soft to run
Yerzley resilience (%)	45′	50.0	53.7	52.4	48.0	46.4	53.9	53.1	54.8	47.5	69.3
% Compression set (ASTM-B)	30′	22.3	32.3	32.1	31.5	36.2	23.7	29.9	31.1	38.3	27.7
	45′	20.2	22.7	23.3	24.5	27.9	18.2	23.3	23.4	28.5	22.5
Crescent tear @ 212° F	15′	137	214	223	No sample	219	215	209	212	105	105
	30′	215	247	161	No sample	268	206	213	166	211	135
	45′	253	188	166	146	268	189	178	156	206	103
	60′	206	168	211	220	294	187	175	188	219	130
Goodyear angle abrasion (cc loss—1200 Rev.)	45′	3.2	5.2	4.7	4.9	4.9	4.5	5.0	5.4	5.0	29.8***
Specific gravity	60′	1.144	1.138	1.140	1.145	1.146	1.131	1.144	1.146	1.148	1.000

*** These samples could only be run for 200 revolutions. The loss at 200 revolutions was multiplied by 6 to obtain the value in the table.

The correlation of "structure" properties with Mooney viscosity or extrusion shrinkage is further complicated by the effect of densification. The oil absorption of carbon black is quite dependent upon densification[38]. Some of this effect of densification upon "structure" properties is removed by using the apparent specific volume under pressure. The effect of densification upon Mooney viscosity[38] and extrusion shrinkage appears to be slight, but apparently definite, approximately equal to the experimental errors in running the tests.

F. THE NORMAL RANGE IN PROPERTIES OF THE VARIOUS TYPES OF RUBBER GRADE CARBON BLACKS

Those who work with carbon blacks need to know how one type of carbon black compares in its properties with other types. The data in Tables II through VII are illustrative, but the values apply only to the specific samples which were tested. It also seems important to try to set out the range of properties which can be expected from various brands of a given type of carbon

TABLE VIII

EXPECTED RANGE IN PRIMARY PROPERTIES FOR VARIOUS TYPES OF RUBBER-GRADE CARBON BLACKS

Type of carbon black	Average E.M. particle diameter, A	BET surface area, m^2/g	% Hydrogen	% Oxygen	"Structure" properties: Mineral oil absorption cc/g	"Structure" properties: Apparent Specific volume @ 734 psi cc/g
MT (Medium Thermal)	2700–5000	6.5–9.1	0.27–.34	0.00–0.10	0.25–0.45	0.75–0.87
FT (Fine Thermal)	1200–1900	13–22	0.40–.50	0.00–0.25	0.40–0.60	0.90–1.05
SRF (Semi-Reinforcing Furnace)	590–860	20–35	0.30–.45	0.15–0.55	0.75–0.90	1.20–1.35
GPF (General Purpose Furnace)	500–650	25–30	0.35–.45	0.15–0.40	0.95–1.05	1.30–1.40
HMF (High Modulus Furance)	460–660	30–45	0.30–.41	0.20–0.35	0.85–1.10	1.20–1.46
FF (Fine Furnace)	400–560	45–75	0.34–.39	0.40–0.60	0.75–0.95	1.20–1.35
FEF (Fast Extrusion Furnace)	310–580	36–48	0.30–.39	0.15–0.65	1.15–1.45	1.40–1.70
HAF (High Abrasion Furnace)	260–350	62–88	0.27–.34	0.50–1.00	1.20–1.40	1.45–1.60
ISAF (Intermediate Super Abrasion Furnace)	175–275	95–135	0.20–.32	0.75–1.45	1.25–1.45	1.45–1.75
SAF (Super Abrasion Furnace)	140–270	120–145	0.28–.34	1.00–2.00	1.30–1.70	1.55–1.75
SCF (Super Conducting Furnace)	160–250	175–225	0.17–.22	0.90–1.20	1.30–1.55	1.60–1.80
EPC (Easy Processing Channel)	290–350	95–125	0.60–.75	2.90–3.50	1.04–1.20	1.49–1.64
MPC (Medium Processing Channel)	240–300	100–135	0.50–.60	2.70–3.60	1.04–1.25	1.49–1.60
HPC (Hard Processing Channel)	230–260	130–160	0.40–.52	2.70–3.60	1.03–1.20	1.50–1.65
CC (Conducting Channel)	175–275	175–420	0.33–.45	2.60–4.00	1.15–1.65	1.50–1.75
ACET (Acetylene)	350–450	55–70	0.06–.09	0.07–0.26	2.50–3.50	1.80–2.20

black. After all, if different brands of carbon black belong in the same classification, then they must have properties which are sufficiently similar to justify their being classified together. Also, it is a fair question to ask just how much variation in properties can be expected from random samples representing different brands of a given type of carbon black.

The author has studied the analyses of hundreds of samples of competitive brands of carbon black and has attempted to set down in tabular form the variations (or uniformity) of the primary properties to be expected. The results of the study are presented in Table VIII. It is believed that well over 90% of the analyses for random samples will fall within the range of values listed in the table. The midpoints of the ranges are believed to be characteristic of the indicated type of carbon black. To a certain extent, the values in the table represent actual variations in the samples tested; but they also represent variations in analytical technique. The author has endeavored to be fair and objective, but it is recognized that in time revisions may be necessary.

The table itself is incomplete without notes of explanation and qualification, and these are set out below.

Average particle diameter: Aside from human and instrumental factors, the chief factor which limits precision of the electron microscopic values is our ability to prepare suitable pictures (electron micrographs) for counting. The techniques of preparing the dispersions differ greatly between laboratories—some laboratories even used "dry mounts" because of the difficulty of preparing suitable dispersions. Values for particle size from one laboratory tend to fit into a pattern which is often different from that of another laboratory. The differences between laboratories become most significant for finely divided, difficultly dispersible samples, particularly the ISAF, SAF, SCF and CC carbon blacks.

% Hydrogen and % oxygen: The values listed are for reasonably fresh samples after drying at 150° C for one hour in a stream of dry nitrogen (10 ml per min) in a microcombustion tube. The analyses for both hydrogen and oxygen tend to increase during normal exposure to the atmosphere. After a year or two, the hydrogen values may increase several hundredths of a per cent. The oxygen values of high surface area samples (100 m^2/g or more) may increase as much as 1%.

Mineral oil absorption: These values were obtained in one laboratory by three different technicians. The end point was taken at the "single ball" stage, e.g., the point at which the oil-black mixture could just be worked into a single stiff ball with a firm spatula. The values are sensitive to differences in densification[38]. While accumulating the data, it has been possible to cross-check several series of samples in two or more laboratories. In these cases, the various sets of data always placed the samples in the same order, although the values obtained for a given sample were frequently quite different.

Apparent specific volume: These values were obtained in a conductivity cell somewhat similar to that described by Balfour, Riley and Robinson[47]. The values are less sensitive to variations in densification than the values for oil absorption.

SRF: Semi-reinforcing furnace blacks are produced at several levels of extractable matter. The nonstaining types contain the least extractable material and have the lowest hydrogen values. The difference in hydrogen contents between the staining and nonstaining varieties is mainly due to differences in the carbon blacks: only a minor part of the differences in hydrogen content can be shown to be due to the tarry, extractable matter, itself.

HMF: There are at least two distinct types of high modulus furnace blacks. They are not strictly interchangeable in many rubber compounds. Statex 93 is higher in "structure" properties than the other brands in this classification.

FEF: Some manufacturers supply fast extrusion furnace blacks in a "high structure" range as well as in a "lower structure" range. However, a part of the differences in "structure" properties in the table are due to differences in densification.

ISAF: The socalled "low modulus" intermediate super abrasion furnace black has hydrogen content of 0.20 ± 0.02%. "High modulus" types range between 0.25 and 0.32%.

IV. THE CHEMISTRY OF CARBON BLACK

A. THE AROMATIC NATURE OF CARBON BLACK

Carbon blacks are invariably formed in a high temperature gas stream, a process involving pyrolysis. Such pyrolysis of aliphatic raw material results in aromatization (ring formation). If the feed stock is a naphthenic or aromatic

oil, the rings are already present in the raw material at the time it enters the furnace. In either case, pyrolysis results in condensation to larger ring systems and dehydrogenation. As more and more rings condense, they form larger and larger units. In addition, these large units tend to come together and arrange themselves into stacks, or crystallites. A layer plane in such a crystallite may contain in the order of 100 carbon atoms, and an average of three or four layer planes may make up a crystallite. These crystallites, from whose edge atoms hydrogen has been removed, by pyrolysis, are quite reactive; and, when two or more crystallites come together, they will adhere. The possibilities for buildup of a chemically linked, regularly organized structure are limited by the time element (time to attain an orderly arrangement) and stearic factors. Continuation of this process results in particle formation from thousands of crystallites. But these particles are not closely packed like a solid brick structure. There has not been sufficient opportunity for alignment and ordering. Vacant spots between the crystallites provide a labyrinth into which most, if not all, chemical reagents are unable to penetrate. This results in some "unfilled valences" where hydrogen has been removed from a carbon atom at the edge of the crystallite during pyrolysis, and no other atom has been available to fulfill its valency requirements. But not all the hydrogen has been removed from the edge atoms of the crystallites—far from it, and this hydrogen is of great importance in determining the properties of the carbon black. *It seems to determine the extent to which the carbon black will react like a polycondensed aromatic hydrocarbon.*

The intense reactivity at the surface under the *conditions of formation* may involve reaction with oxygen-containing gases, like carbon monoxide, carbon dioxide and water, which are present in the gas stream; but this appears to be of small importance in determining the oxygen content of the finished sample. Rather, it appears to result in etching of the surface, producing carbons with higher surface areas as determined by adsorption techniques than would be expected from electron microscopic examination.

After carbon black formation has taken place—generally in a small fraction of a second—the gas stream is quenched. In some operations this avoids further buildup of carbon which would produce a larger particle size. In other operations excessive etching by oxygen containing gases in the furnace is avoided. In either case excessive dehydrogenation is prevented. The carbon black at this stage contains very little oxygen—a furnace black like Philblack O (HAF) might have 0.15% oxygen. Further handling in the plant by conveyors, micropulverizers and pellet mills, etc., results in a pickup of oxygen to the 0.5 to 0.8% range. By the time it reaches the customer's plant, this value will generally fall between 0.65 and 1.0%. Only on prolonged storage (a matter of years) will its value increase above 1%, and here the moisture in the air is probably a critical factor. Such increase in oxygen content on storage may well be associated with a very small increase in surface area, since the maximum in oxygen content (cf. Figure 7) which freshly prepared HAF samples will attain rarely exceeds 1%; and a slow etching by oxidation would very likely have to take place before the oxygen content would exceed this value. A large part of the increase in oxygen content takes place during the pelleting operation if dry pelleting is employed, or during the drying if the product is wet pelleted.

We can, then, think of carbon blacks chemically as being somewhat like a series of degraded polycyclic aromatic hydrocarbons at various states of oxidation. By "degraded" we mean that the condensation of atoms into layers may

not be perfectly regular. Holes may develop where carbon atoms may be absent. Foreign atoms like sulfur may take the place of a carbon atom in a layer plane. The valences of the edge atoms of the layer planes are not completely satisfied with their normal complement of hydrogen atoms. In addition, the rapid condensation of crystallites into the particle probably does not permit establishing regular carbon-carbon bonds at normal angles, and strain in bond angles seems inevitable. Some warping of the layer planes is also decidedly possible.

Aromatic hydrocarbons are not unreactive materials. In a series of polycondensed aromatic compounds, as the number of rings is increased, the aromatic bonds become more like olefinic double bonds, e.g., the bond order increases. Reagents which add to double bonds in the ethylenic compounds react with benzene almost exclusively by *substitution*; but, we we move along the series, naphthalene, anthracene, naphacene, etc., *addition reactions* become more and more important[48,49]. *Affinity for free methyl radicals* increases[50], and there is a greater tendency to form *molecular complexes* with a variety of materials including polynitro compounds, quinones, halogen molecules and even silver ions[48]. Aromatic hydrocarbons are Lewis bases (electron donors), and this property increases with increasing number of aromatic rings in the molecule. (A large number of papers have appeared on this subject during the past ten years; References 51, 52, 53, 54 and 55 are of interest but not meant to be a complete bibliography.) According to Longuet-Higgins[56], the proton affinity (a measure of basicity) of benzenoid hydrocarbons containing no odd membered rings should parallel their free radical affinity. Indeed, addition complexes form between aromatic hydrocarbons and such Lewis acids (electron acceptors) as aluminum chloride, antimony trichloride, stannic chloride, halogens[48(p.85)] etc. Another indication of the basic character of aromatic hydrocarbons is the fact that they dissolve in anhydrous hydrogen fluoride. Many polycyclic aromatic hydrocarbons are extremely reactive materials; this reactivity makes it difficult to prepare them in a high state of purity. Hence, to the extent that carbon blacks resemble these polycyclic hydrocarbons, we would expect a high order of reactivity by substitutive, additive and complexing reactions. An organic chemist might look upon this reactivity as the very essence of several important types of chemisorption.

We will return to this matter of chemical reactivity again in Section IV, D where we will mention some features of it which seem to be worth consideration in regard to the effect of carbon black upon the molecules and intermediates which are present in a rubber stock during vulcanization.

B. THE ULTIMATE STRUCTURE OF CARBON BLACK

X-ray analysis of carbon black shows it to be largely organized into crystallites[57] which, on the average, are composed of three or four parallel layer planes. (Acetylene black is an exception. In it, about seven layer planes are present in an average crystallite.) Within the layer planes, each carbon atom is surrounded by three other carbon atoms, like the carbon atoms in graphite[58] or an internal carbon atom in pyrene. The layer planes are generally some 15 to 25 A across (L_a dimension) and are separated by distances of roughly 3.5 A (c/2 dimension). Hence, the crystallite heights (L_c dimensions) range from about 15 A to a maximum of 25 A (acetylene black). No evidence for orientation of the parallel layers about their normal can be found in commercial carbon blacks[57,58].

It appears that some of the layer planes are not parallel to the layer planes near them[59]. These are referred to as "single layers". In addition, some of the carbon is evidently not oriented in the graphitic structure at all. It is called "nonoriented" or "random" carbon. Such random carbon might be present as short aliphatic groups attached to the oriented carbon edge atoms, perhaps forming chemical bonds which hold crystallites, their layer planes and the single layers firmly fixed with respect to each other. It could also be present as attached aliphatic methyl groups or chains; but such chains, if present at all, would surely be short. Thus, random carbon refers to any carbon not oriented in a plane similar to the orientation within a layer of graphite.

This picture of the ultimate structure of the carbon black particle is a result of very precise x-ray analysis conducted in several laboratories, principally by B. E. Warren[60,61,62], L. Alexander[63], A. E. Austin[64,65] and others. Some recent values obtained by A. E. Austin on the same samples of Table II are listed in Table V. X-ray techniques have been markedly improved in recent years, and their value has increased accordingly. Until recently the L_a values, for instance, were not sufficiently precise to justify their use in any but the most general considerations.

The values of layer dimension, L_a, obtained from the (10) and (11) bands should agree if the broadness of the band is essentially a function of layer size alone. However, for many of the carbon blacks, L_a from (10) was greater than from (11). Austin believes that this effect is due to a distortion within the layers. Such distortion may be produced by a vacancy or impurity atom. Thermal blacks appear to have the greatest amount of disorder within their layer planes. Acetylene black seems to exhibit very little intralayer disorder. This is also found in the case of the oil blacks, Philblack A, Philblack O, Philblack I and Philblack E, of Table V.

Hydrogen is such an important constituent of carbon black that it is important to try to determine just where it is located in the structure. We might speculate that it is bound mainly to one or more of the following types of carbon atoms: edge atoms of the parallel layers, edge atoms of the single layers, randomly oriented carbon atoms and possibly at points of discontinuity within the layer planes. Austin[65] has endeavored to obtain an indication from his data as to which of these carbon atoms is combined with the hydrogen atoms.

By plotting the *per cent of carbon in the edges of the parallel planes* against the *atomic per cent hydrogen*, it was found that data for all channel type carbons examined fell close to a line representing approximately one hydrogen atom for every 3.2 carbon atoms at the edges of the parallel layers. It seems possible that for channel blacks this relation indicates the predominant location of the hydrogen in the samples.

No such relationship could be demonstrated for furnace blacks made from oil. However, when the *atomic per cent hydrogen* was plotted against *the sum of the carbon in random orientation, plus carbon in edges of single layers*, all furnace blacks made from oil and acetylene black fell close to a line (four such carbon atoms per hydrogen atom). Austin suggests that furnace blacks made from oil have their hydrogen concentrated in the random carbon.

The plots of data for thermal blacks (P-33 and Thermax) and all furnace blacks made from gas were less definite; but, in general, these materials seemed to be much more closely related to the channel blacks than to the oil furnace blacks.

Such plots should be interpreted with caution. But they seem to indicate that definite structural differences exist between furnace blacks made from oil

and acetylene on the one hand and those made from gas on the other. The hydrogen content of the various types of carbon appears to be distributed in somewhat different ratios between the various possible types of carbon atoms. The relatively small amount of hydrogen associated with the oxygen at the surface of the carbon black particles is neglected in this section.

C. THE NATURE OF THE OXYGEN–CONTAINING GROUPS

It would be desirable to know the manner in which the oxygen in carbon black is combined. However, it has not been possible to quantitatively account for the larger part of it.

Villars[66] studied the reaction between various samples of carbon black and the Grignard reagent and reported that approximately 26% of the total oxygen on the carbon black surface is reactive toward this reagent. What is deter-

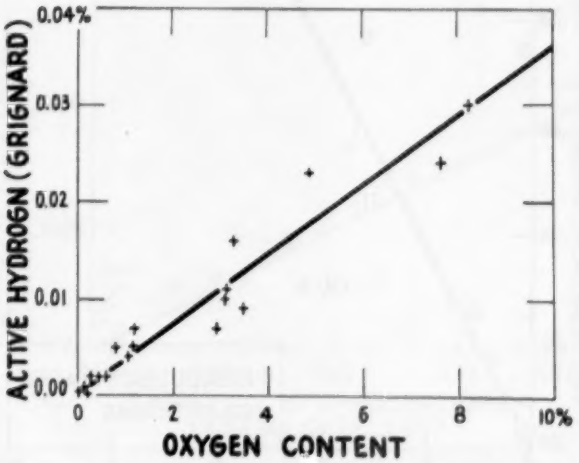


FIG. 14.—Graph showing that the active hydrogen measured with the Grignard reagent is proportional to the total oxygen content of commercial carbon blacks.

mined in this procedure is the methane evolved and the total reagent consumed. From the quantity of methane evolved, Villars reported that roughly 14% of the oxygen is attached to an active hydrogen, presumably as —COOH or —OH groups. Some of the Grignard reagent was consumed without methane evolution, which indicates the presence of other groups, possibly aldehyde, ketone or quinone.

E. W. D. Huffman has made certain improvements in the Grignard technique so the sample can be dried in a stream of nitrogen at 150° C and transferred to the reagent without exposing it to the atmosphere. Values for active hydrogen obtained by this procedure are listed in Table III and plotted against total oxygen content of the sample in Figure 14. According to these measurements, approximately 5.6% of the total oxygen is associated with active hydrogen.

Smith and Schaeffer[67] reported that a variety of oxygen-containing groups can be found by emission spectra in the decomposition products of carbon black

bombarded with electrons in a vacuum. Among these groups are C—H, —CHO, —OH, —COOH and —C=O. However, it was not possible to make a quantitative comparison of the amounts of these groups on a given sample.

An attempt to analyze oxygen-containing groups on the surface with the active reagent, diazomethane[68], indicated the presence of —OH and —COOH groups. During the treatment, the nitrogen contents of the samples increase. This indicates, but not conclusively, the possibility of 1,4-quinone groups. If quinone groups are present, the carbon black should take up hydrogen readily in the presence of the Adams catalyst—two hydrogen atoms should be taken

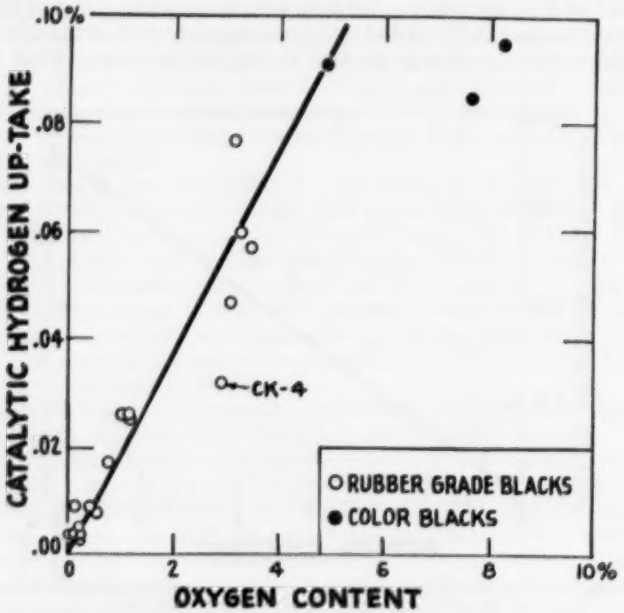


FIG. 15.—Graph showing proportionality between hydrogen uptake in the presence of the Adams catalyst and the total oxygen content of the samples.

up for each quinone-type oxygen atom present. This is a reasonably reproducible quantitative procedure for determining quinone groups on carbon black. Data are reported for the carbons in Table III. The catalytic hydrogen uptake is plotted against total oxygen content in Figure 15. From the data, it is concluded that 15% of the oxygen present on the surface of carbon black reacts like 1,4-quionone groups. Lindberg and Paju[69] have shown that sodium borohydride reduces quinones quantitatively to hydroquinones, one hydrogen atom adding to the sample for each quinone-type oxygen atom. (Nucleus hydrogenation was found by Lindberg and Paju only in the case of dihydroxyquinones.) The correlation[68] between catalytic hydrogenation and sodium borohydride reduction is gratifying, almost exactly as predicted, Figure 16.

Recently Hallum[70] has studied the oxygen-containing groups on carbon black, principally by infrared and polarographic techniques. He interprets his

results as showing the presence of hydrogen-bonded, aromatic hydroxyl and quinone groups.

Garten and Weiss[71] suggested that the oxygen content of carbon blacks possess the properties of seimiquiones and later[72] suggested that some of the oxygen occurs as "a lactone which is present in conjunction with a phenol such as occurs in the fluorescein and phthalein dyestuffs". (The quotation is taken from the abstract of their paper.)

Cole and Dannenberg[73], employing an interesting infrared technique, report "strong evidence for . . . the presence of hydroxyl, carboxyl and ketonic groups on the carbon black surface". They also found "an extremely stable structure, absorbing near 6.3 microns, believed to be a conjugated chelate, the result of interaction of beta-situated ketonic groups and/or beta-situated

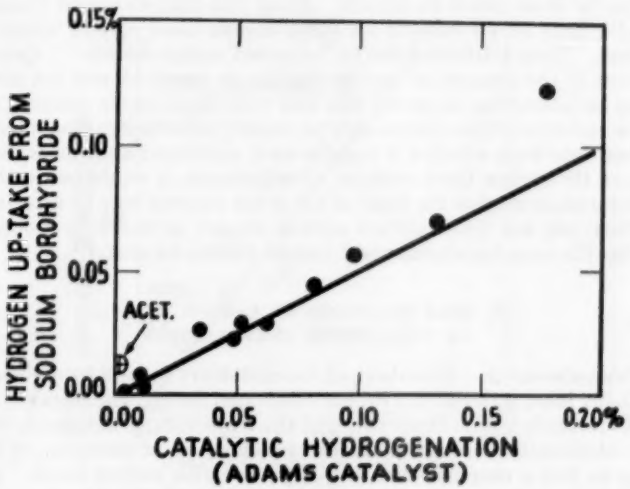


FIG. 16.—The proportionality between catalytic and sodium borohydride hyrdogenation.

hydroxy and ketonic groups". This appears to be the same structure which Hallum found and referred to as "hydrogen-bonded aromatic hydroxyl and quinone groups". Cole and Dannenberg report that they found no evidence for quinone groups.

Whatever their exact nature, approximately 15% of the oxygen on the surface of carbon black seems to react with sodium borohydride and with hydrogen in the presence of the Adams catalyst like quinones. Also, the increase in nitrogen content on treatment with diazomethane, though leaving much to be desired from a quantitative point of view, suggests the presence of these groups. Barton *et al.*[46], from their experiments on carbon black-rubber interaction and the oxidation of ferrous ions, suggested that their experiments might be accounted for by the presence of quinone groups on the carbon black surface. The subject is under intense study by several laboratories, but qualitative evidence is still inconclusive.

Probably the least satisfactory position, with respect to group analysis, is the question of presence or absence of carboxyl groups. Satisfactory qualita-

tive tests need to be developed; and, if definite evidence for the presence of these groups can be obtained, quantitative tests will no doubt be developed.

The proportionality between total oxygen content and the amount of oxygen associated with active hydrogen on the one hand and between total oxygen and "quinone" type oxygen, as measured by catalytic hydrogenation, on the other is somewhat disconcerting. It makes it more difficult to determine which of the two types of oxygen are responsible for the effects associated with rubber properties. Here, a certain amount of chemical common sense is the only solution at present.

Another grave problem is associated with the oxygen which has not been identified by group analyses. This apparently is the majority of the surface oxygen. Perhaps we can find some solace in the belief that, with the techniques employed so far, we have been working with that oxygen which would be expected to be most active in rubber. Along this line, Cole and Dannenberg[73] reported a band at 4.3 microns for every carbon black sample which they investigated. They attributed this to "adsorbed carbon dioxide". Quantitative evaluation of the amount of carbon dioxide so adsorbed was not attempted. It would be interesting to pursue this lead with experiments designed to determine the stability of this presumably physically adsorbed carbon dioxide[74] and to further determine whether it constitutes a significant amount of the oxygen present on the carbon black surface. Furthermore, it would be worthwhile to try to determine whether the band at 6.3 or 6.4 microns may be associated with the carboxylate ion (chemisorbed carbon dioxide or carboxyl groups) as reported by Eischens for chemisorbed carbon dioxide on nickel[74].

D. SOME REACTIONS OF CARBON BLACK AT VULCANIZING TEMPERATURES

1. General remarks.—It has been all too customary to consider carbon black as a chemically inert material in a rubber compound during vulcanization. Nothing could be farther from the truth. At the temperatures commonly employed during vulcanization, carbon black reacts with a host of materials; in fact, it is not easy to find a reagent which will not react with carbon black. A rubber compound during vulcanization provides carbon black with many reactive compounds and intermediates. It would be surprising if it did not find a number of molecules, radicals and even ions with which to react. Most, if not all, of the reactions with which we are concerned appear to take place almost exclusively at the surface, and special techniques are necessary to follow them. This is the very essence of an important type of surface chemistry, chemisorption and catalysis.

This section on reactions which can take place at times and temperatures commonly used during vulcanization is necessarily limited by the scope of available data, and the examples chosen are illustrative.

It appears evident that at 150° C, say, carbon black possesses several important types of reactivity. Prominent among them are:

(1) The reactivity which is determined by its hydrogen content and which resembles the reactivity of condensed, polycyclic, aromatic hydrocarbons.

(2) The reactivity which is determined by its oxygen content, more specifically (a) by that portion of its oxygen content which reacts like 1,4-quinone type oxygen (as measured by catalytic hydrogenation at atmospheric temperature and pressure in the presence of the Adams, reduced platinum oxide, catalyst)

and (b) that portion which is associated with active hydrogen (measured by the Grignard reagent).

The extent of the reactivity of carbon black at vulcanizing temperatures with compounds containing —SH groups, like hydrogen sulfide[75] (Section IV, D, 3) and probably mercaptans, seems to be mainly dependent upon the content of quinone-type oxygen in the sample. The reactivity with compounds containing NH groups, like ammonia, dimethylamine, etc., seems to be dependent upon both of these active types of oxygen (see Section IV, 5, D).

(3) A third type of reactivity involves chemisorption. Carbon black has a very pronounced affinity for materials containing hydrogen, like water[76], and at least some hydrocarbons (Section IV, D, 7), and very likely a multitude of

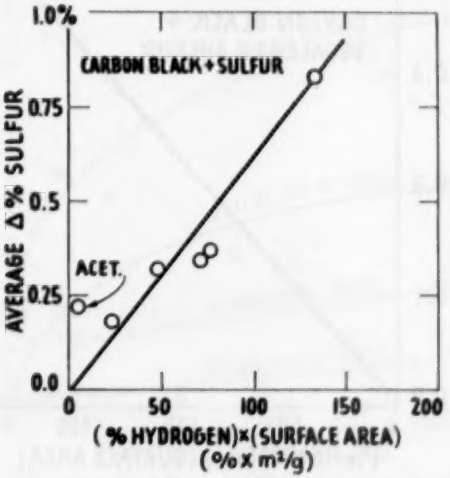


FIG. 17.—The increase in sulfur content increases with the product of the hydrogen content and the surface area of the carbon blacks when they are heated with sulfur.

others. These molecules are apparently chemisorbed with partial or complete dissociation into neutral hydrogen atoms and radicals. (In some cases the dissociation may be into protons and ions.) It seems highly probable that similar chemisorption with dissociation takes place with compounds containing —O—O—, —S—S— and other linkages. This chemisorption is regarded as a necessary first step in the catalysis of decomposition of hydrogen peroxide, benzoyl peroxide, dicumyl peroxide and possibly of tetramethylthiuram disulfide as discussed in Section V, D. It may also be important in the action of carbon black as a catalyst for dehydrogenation by sulfur (Section V, C, 1) where the chemisorption may involve the molecule which is being dehydrogenated and the sulfur molecules—a step in opening of S_8 rings.

(4) A fourth type of reactivity is represented by the ion-exchange properties of carbon black. The most important aspect of this during vulcanization probably determines its interaction with soluble zinc salts in the rubber mix (Section V, F).

2. Reaction with sulfur.—When carbon black reacts with sulfur, hydrogen sulfide is evolved, and the resulting carbons contain sulfur which cannot be removed by extraction with solvents for sulfur[75]. In this reaction, carbon black behaves similar to an aromatic hydrocarbon. The reaction between sulfur and carbon black involves dehydrogenation of the carbon black; hence, the hydrogen content of the carbon black is one of the important factors in determining the amount of sulfur which is added to the sample. However, as one might expect, the surface area which is exposed to the reagent is also important. If various rubber grade carbon blacks be treated with sulfur at 150° C for one hour and then toluene extracted for 30 days to remove the unreacted sulfur, the increases in sulfur contents are proportional to the products of the hydrogen

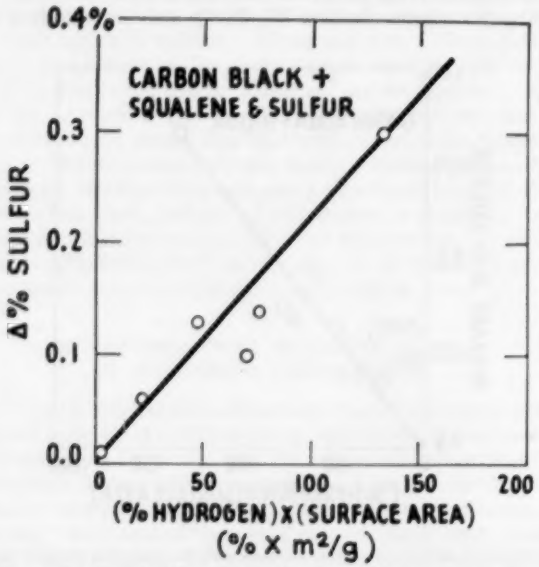


FIG. 18.—The increase in sulfur content increases with the product of the hydrogen content and the surface area of the carbon blacks when they are heated with solutions of sulfur in squalene.

contents times the respective surface areas of the samples[77], Figure 17. The oxygen contents of the carbon blacks tend to reduce the amounts of sulfur which combine; and, hence, the values for the channel type carbons are slightly lower than for furnace blacks whose (% hydrogen) × (surface area) values are comparable. Quite similar reactivity of sulfur with carbon black is observed when carbon black, squalene (a hydrocarbon composed of condensed isoprene units) and sulfur are heated together, Figure 18. In this case, it is not known whether the sulfur is combined exclusively with the carbon black, exclusively with the "bound squalene" or whether it forms sulfur bridges connecting the carbon black and squalene molecules.

Although carbon black seems to have considerable beneficial effects on the interaction between sulfur and rubber during vulcanization, the reaction between carbon black and sulfur described here may very well be an unavoidable side reaction of no definite benefit to a vulcanized stock. On the contrary, it

may remove sulfur from the vulcanizing system which could otherwise take part in the reactions leading to the crosslinking of rubber molecules. However, the reaction between sulfur and carbon black in rubber might very well produce

$$\diagdown\!\!\diagup \text{C—S}\cdot \text{ radicals or } \diagdown\!\!\diagup \text{C—SH}$$

groups which would be capable of reacting with rubber molecules at the carbon black surface. This would result in a carbon black-sulfur-rubber molecule crosslink which would firmly anchor rubber molecules to the carbon black surface. Unless these were the main, or only, mode of anchoring rubber molecules to the carbon black particle, a consideration which seems quite unlikely, little or no beneficial contribution to the reinforced rubber would result.

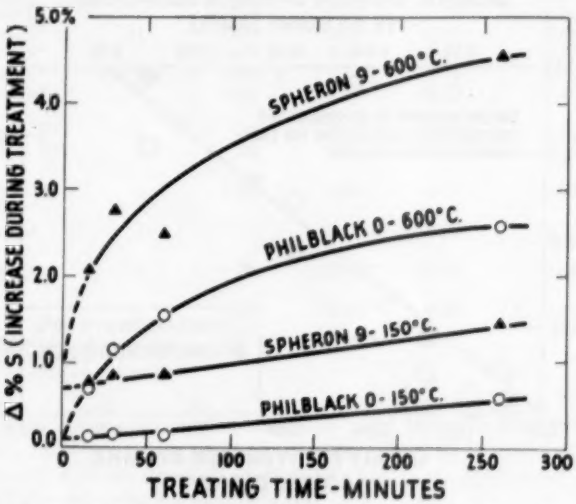


FIG. 19.—The increase in sulfur contents of carbon blacks with time at two temperatures when treated with hydrogen sulfide.

3. Reaction with hydrogen sulfide.—The reaction(s) between carbon black and hydrogen sulfide[75] are of some interest to the overall picture of reinforcement because hydrogen sulfide is always present when rubber is vulcanized with sulfur or sulfur-containing materials like tetramethylthiuram disulfide. The increase in the sulfur content of two carbon blacks, Philblack O (HAF) and Spheron 9 (EPC), when heated in hydrogen sulfide at 150° and 600° C, is shown as a function of time of treatment in Figure 19[75]. The 150° curves do not extrapolate to Δ%S values of zero at zero treating time, and it was suggested that at 150°, at least, two types of reaction were taking place—a rapid reaction and a slow reaction which is believed to be of minor importance in our considerations here. (The surface area of the carbon black and its hydrogen content may very well be the dominant factors in determining the extent of this slow reaction.)

The extent of the rapid reaction is directly proportional to the amount of hydrogen which reacts with carbon black at room temperature in the presence of the Adams (reduced platinum oxide) catalyst. It was suggested that the

carbon black contains 1,4-quinoid groups which are involved in both the rapid hydrogen sulfide reaction and the catalytic hydrogenation. Accordingly, correlation between catalytic hydrogenation and increase in sulfur content at short heating times might be expected. This correlation is demonstrated in Figure 20. Here values for 15 and 30-minute hydrogen sulfide treatments are plotted; the experimental setup was not designed to control treating time for such short periods, and no significant differences in the two sets of values could be expected. The correlation is gratifying, and the line drawn in the figure represents the addition of one sulfur atom for each quinone-type oxygen atom as measured by the catalytic hydrogenation. Some consequences of this reaction with hydrogen sulfide will be discussed in Sections V, C and V, F.

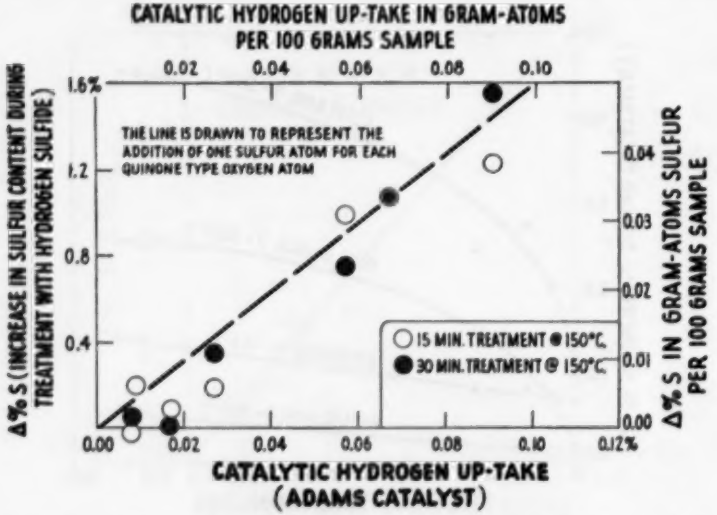


FIG. 20.—The rapid increase in sulfur content when various carbon blacks are treated with hydrogen sulfide at 150° C is stoichiometrically related to their quinone content as measured by catalytic hydrogenation.

4. Reaction with carbon disulfide.—Carbon disulfide is evolved in considerable quantities when rubber is vulcanized with TMTD. Hence, it was considered desirable to make a very limited study of the interaction between carbon black and carbon disulfide. A series of carbon black samples were heated with carbon disulfide in micro Carius tubes at 150° C. After cooling, the tubes were opened and evacuated over night. The samples were then dried for one hour at 70° C in a stream of dry nitrogen and analyzed for sulfur content. The sulfur contents of the untreated samples, the treated samples and the increase in sulfur contents during treatments are listed in Table IX. The increases in sulfur content are small in most cases; the two exceptions were Spheron 9 (EPC) and Philblack E (SAF). These two samples were old samples, approximately five years old, and had not been protected in any way from the atmosphere. The other samples were approximately one year old and had been kept in bottles which no doubt reduced the effects of exposure to the atmosphere. It is quite possible that the carbon black catalyzed the

TABLE IX

THE INCREASE IN SULFUR CONTENT OF CARBON BLACK SAMPLES TREATED FOR ONE HOUR WITH CARBON DISULFIDE

Sample	Drying time, hours	Drying temp. (° C)	Sulfur content		Increase in sulfur content (Δ%S)
			Untreated	Treated	
Philblack O*	1	ca. 30°	0.43	0.66	0.23
Philblack O*	1	70	0.43	0.68	0.25
Philblack O*	1	150	0.43	0.63	0.20
Philblack O*	24	150	0.43	0.47	0.04
Philblack O*	1	300	0.43	0.38	− .05
Philblack O*	1	600	0.43	0.38	− .05
Spheron 9*	1	ca. 30°	0.03	1.79	1.76
Spheron 9*	1	70	0.03	1.74	1.71
Spheron 9*	1	150	0.03	1.03	1.00
Spheron 9*	24	150	0.03	0.50	0.47
Spheron 9*	1	300	0.03	0.14	0.11
Spheron 9*	1	600	0.03	0.93	0.71
Spheron 9*	1	600	0.03	0.13	0.10**
Philblack E*	1	70	0.35	2.16	1.81
Philblack E*	1	70	0.35	2.34	1.99***
Philblack A	1	70	0.67	0.75	0.08
Spheron 4	1	70	0.00	0.32	0.23
Shawinigan	1	70	0.02	0.08	0.06
Elf O	1	70	0.10	0.38	0.28

* Not the same sample which is listed in Tables II through VIII.
** Repeat of analysis only.
*** Repeat of preparation and analysis.

reaction between water and carbon disulfide[78] and that the abnormally high sulfur contents of the two older samples do not reflect an interaction between the carbons and carbon disulfide, but rather with its hydrolysis products (hydrogen sulfide and possibly even sulfur).

TABLE X

THE INCREASE IN NITROGEN CONTENT OF CARBON BLACK ON TREATMENT WITH DIMETHYL AMINE

Carbon black	% Active hydrogen (Grignard)	% Catalytic hydrogen up-take (Adams catalyst)	Nitrogen content after treatment*	
			Drying time at 150° C	
			1 hour	24 hours
Philblack A	0.002%	0.008%	0.12%	—
Philblack O	0.005	0.017	0.21	0.20%
Philblack E**	0.009	0.034	0.56	—
Spheron 9**	0.009	0.062	0.59	0.58
Spheron 4	0.016	0.064***	0.79	—
Acetylene Black	0.000	0.009	0.09	—
Elf O	0.023	0.091	0.93	—

* Assays on the untreated samples of Philblack O and Spheron 9 showed 0.00% nitrogen by the sealed tube Kjeldahl procedure.
** Not the same samples of Tables II through VII.
*** This value differs slightly from that in Table III. It was run at the time of the treatment with dimethylamine.

These experiments are interesting in pointing out how carbon black can, and no doubt does, react with or strongly adsorb intermediates formed during vulcanization and suggest additional facets of an already complicated system.

5. Reaction with ammonia and dimethylamine.—Carbon black reacts with ammonia[75]; the extent of the reaction during a given treatment at vulcanizing temperatures seems to be dependent on the oxygen content of the sample. The data of Anderson and Emmett[79] suggest that both ammonia and methylamine are chemisorbed by carbon black at temperatures considerably below those commonly employed in vulcanization.

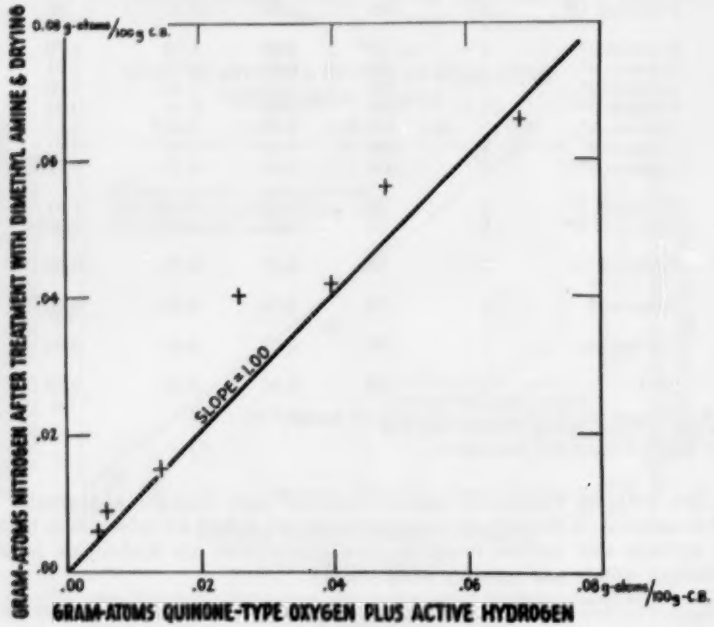


FIG. 21.—The in crease innitrogen content for various carbon blacks when treated with dimethylamine is related to their active hydrogen and quinone contents.

When rubber is vulcanized with tetramethylthiuram disulfide (TMTD), diemthlyamine is found in the reaction products[80]. Hence, it is of interest to compare the increases in nitrogen content of various carbon blacks following treatment with dimethylamine at 150° C, Table X. The samples were heated with dimethylamine in an unsealed Carius tube in a steel bomb. The bomb was placed in an oven which had been preheated to 150° C. Time was allowed for a thermometer which was in contact with the bomb to register 150° (45 to 60 min), and the treatment was allowed to continue for one hour at 150°. The bomb was removed from the oven, cooled and opened and the Carius tube placed in a vacuum desiccator over P_2O_5 and the vacuum maintained by pumping for 18 hours. The sample was used in this condition for drying and analysis. On opening the bomb, a strong orod of ammonia was observed.

The gram-atoms of nitrogen found in a given treated sample is approximately equal to the sum of the gram-atoms of 1,4-quinone type oxygen, as

measured by catalytic hydrogenation, and the active hydrogen, as measured with the Grignard reagent, Figure 20.

6. The affinity of carbon black for the nitrogenous materials in natural rubber. —When a carbon black-natural rubber masterbatch is "cured" at vulcanizing temperatures, then subjected to oxidative degradation in *o*-dichlorobenzene through which air is bubbled, the carbon black can be removed by filtration. The nitrogen content of such carbon black is increased. Presumably protein or protein degradation products are removed from the rubber. For instance, a series of masterbatches were made up containing 100 parts smoked sheets (0.35% nitrogen) and 50 parts carbon black. The masterbataches were press "cured" for 30 minutes at 287° F. The masterbatches were then digested four times, 96 hours per treatment, with boiling *o*-dichlorobenzene through which air was bubbled. The samples were filtered to remove decomposed rubber after each treatment. They were then extracted twice, 48 hours each time, with hot (176° C) *o*-dichlorobenzene, and finally for four days with carbon tetrachloride. After vacuum drying (48 hours at room temperature) and nitrogen drying (one hour at 150° C), the carbon blacks were analyzed for carbon, hydrogen, sulfur, ash and nitrogen. The values are listed in Table XI. The car-

TABLE XI

INCREASE IN HYDROGEN CONTENTS (Δ% HYDROGEN) AND NITROGEN CONTENTS OF CARBON BLACKS REMOVED BY OXIDATIVE DEGRADATION FROM "CURED" CARBON BLACK–NATURAL RUBBER MASTERBATCHES

Sample*	% Nitrogen	Δ% Hydrogen
Philblack O	0.45	0.38
Philblack E	0.42	0.78
Spheron 9	0.45	0.53
Spheron 4	0.49	0.63
Shawinigan	0.42	0.35
Elf O	0.50	0.66

* The properties of these carbon black samples are tabulated in Tables II through VIII.

bons removed, no doubt by chemical combination, some 60 to 72% of the nitrogen present in the raw rubber. The importance of the data in the preceding two sections is that they point to a considerable affinity of carbon blacks for nitrogen-containing materials. All commonly used accelerators contain nitrogen, and the affinity of carbon black for such materials is very likely of importance in vulcanization of carbon black-filled rubber stocks. We will return to this subject again (Section V, E).

7. Reaction with rubber and similar hydrocarbons.—So far we have pointed to several types of reaction of carbon black with materials which might be expected to be present in some rubber compounds when they are being vulcanized. We should also consider the question: Does carbon black react with rubber itself?

Carbon black displays a very great affinity for the rubber. Thus, the common natural and synthetic rubbers are irreversibly adsorbed from solution by reinforcing carbons at room temperature[81]. Or if a vulcanized latex sheet be suspended in a slurry of carbon black in water, some of the carbon deposits on the latex. This carbon is held so firmly to the rubber that it cannot be removed, as by scrubbing with soap and water. The amount of carbon black held on the vulcanized latex surface seems to be greater for small particle size, high

structure carbon blacks. A. C. Wolfe, in collaboration with the author, conducted many experiments on this phenomenon.

When carbon black is mixed with a solution of rubber in a ball mill and the solvent removed by freeze drying, a considerable portion of the rubber is found to be insoluble[82]. Merely passing this masterbatch through tight rolls of a roll mill increases the amount of insoluble rubber. Pike and Watson[62] have shown that, during milling, rubber molecules are broken, forming free radicals. These can react with the carbon black surface, the rubber fragments become chemically attached to the carbon black surface and an insoluble gel is formed. In the presence of powerful free radical acceptors, the effect becomes negligible, since the free radicals formed by rupture of rubber molecules react with these free radical acceptors before they can reach the carbon black surface.

As pointed out by J. W. Watson[84], W. F. Watson's[82] experiments showed that the slight milling merely *increased* the insoluble rubber; a considerable amount of it was present after the ball milling of rubber solutions containing carbon black and freeze drying.

When rubber is mixed with carbon black in an open roll mill or in a Banbury mixer, a substantial portion of the rubber becomes insoluble. This insoluble rubber is called "bound rubber". The amount of bound rubber increases as the masterbatch is aged. The quantity of bound rubber on reinforcing carbon black generally represents some 30 to 60% of the weight of the carbon black.

If the mixing is conducted at sufficiently high temperatures, generally in the range of 300 to 400° F, and for sufficient times, say for 30 minutes at the lower temperature, there can be further interaction between the carbon black and the rubber[42–46]. This interaction results in breaking up of the agglomerates of carbon black which are normally present in rubber. (The carbon black particles in such agglomerates are believed to be wetted by rubber, but their persistence is apparently due to the action of the same forces which give rise to agglomeration of carbon black in gases and liquids.) At any rate, the physical properties of the rubber vulcanizates which are prepared from such masterbatches show higher resilience, higher moduli at elongations of 300% or more, lower moduli at low elongations and considerably higher resistivities than would be the case for masterbatches not hot mixed[85]. To observe this effect of carbon black-rubber interaction, the carbon black must contain oxygen on the surface or else promoters, for instance sulfur, must be present during the high temperature mixing. Barton *et al.*, working with natural rubber, estimated the activation energy of the process to be 18 kilocalories per mole[46]. Rehner and Gessler[45], working with butyl rubber, found an activation energy of 16 kilocalories per mole; and Kraus and Dugone[81], using SBR type rubber, found the average activation energy for four blacks to be 18 kilocalories per mole. These activation energies are sufficiently large to indicate that chemical reaction (chemisorption) is taking place.

Although the literature contains many data on bound rubber, there is no really definitive work which thoroughly describes the nature of the phenomenon. Most of the experiments are concerned with the factors which contribute to building it up; little has been reported on what is necessary to remove it from the carbon black. Along this line, the hydrogen contents of the samples removed from "cured" natural rubber masterbatches, Table XI, are of interest. This was no ordinary extraction! It is more than sufficiently vigorous to degrade gum stocks. Yet, judging by the increases in hydrogen contents, the amount of rubber held on the carbon black surface following the oxidative degradation is in the range of some 3 to 7.5% of the weight of the carbon black.

Incidentally, the increases in hydrogen content for the carbons removed from these masterbatches are quite similar to the values obtained from TMTD ("sulfurless") cures plotted in Figure 32 (cf. Section V, G). This rubber is very tightly held. It would be quite desirable to subject this bound rubber problem to techniques like thermogravimetric analysis, with analysis of the samples after the heating process.

Certainly the phenomena described in this section indicate strong carbon black-rubber interaction. The treatments used by different observers differ, and it is not surprising that the results between different laboratories are not generally applicable to those obtained elsewhere. But all seem to be observing different aspects of the same general phenomenon—a chemisorption of rubber by carbon black, or a chemical reaction between the rubber and carbon black surface which in such a system would probably be two ways of referring to the same thing. This interaction appears to be possible when radicals formed by mechanical rupture of rubber molecules contact the carbon black, but this does not appear to be a necessary condition. Chemisorption of a molecule always involves partial or complete dissociation. It seems likely that such dissociation of rubber molecules will take place when rubber is in contact with carbon black, leading to radical formation from the chemisorbed molecules on the carbon black surface. Heat, of course, would be expected to promote such a chemisorptive process.

There are a number of references in the literature which describe chemisorptive interactions between carbon black, or its chemical cousin, charcoal, with hydrocarbons of lower molecular weight than rubber. For instance, Polley, Schaeffer and Smith[86] presented convincing evidence that the medium processing channel black, Spheron 6, chemisorbed dihydromyrcene (an isoprenoid hydrocarbon) at 100° C. When various carbon blacks are heated with squalene, another hydrocarbon composed of condensed isoprene units, extracted for 30 days with toluene, dried and analyzed, an increase in hydrogen content of the carbon black is found which indicates that several per cent of squalene remained on the carbon black surface[77]. Such prolonged extraction with toluene would surely remove any squalene which was not chemically bound to the carbon surface. Such carbon black-hydrocarbon interaction even takes place when carbon black is merely extracted for a prolonged period with toluene[77].

Polley, Schaeffer and Smith[87] also observed that those carbons which interact with butyl during high temperature treatment, e.g., channel blacks, chemisorbe butene-1 at 109° C and isomerize it to *cis*-butene-2. Charcoal is a catalyst for many hydrocarbon conversions, and chemisorption is apparently a prerequisite for most, if not all, of these[88].

It is of interest to note that Johns and Elton[88] found that purified charcoal would adsorb an estimated one to two monolayers of decalin at 90° C which could not be removed unchanged. Instead, what was removed by extraction was the dehydrogenated material, naphthalene. Benzene would remove the naphthalene but not ether or carbon tetrachloride. The amount of naphthalene formed was dependent upon temperature but was independent of the time of residence on the charcoal. Here, decalin is evidently chemisorbed with dissociation of hydrogen from the molecule leaving the dehydrogenated product, e.g., naphthalene. If a rubber molecule were similarly chemisorbed with dissociation of a hydrogen atom, a rubber radical would result, which might be expected to react with and become chemically attached to the carbon black surface. Alternately, one might expect that under suitable conditions such radicals might initiate polymerization of rubber molecules in their vicinity.

Stickney and coworkers[89] suggested "that bound rubber formation is polymer gel formation initiated catalytically by carbon black".

8. Carbon black as a free radical acceptor.—W. F. Watson's convincing demonstration that carbon black reacts with (accepts) mechanically broken rubber molecules which are evidently free radicals[92] was mentioned in Section IV, D, 7. Garten and Sutherland[90] claimed to be studying the free radical acceptor ability of carbon black by heating it with solutions of potassium persulfate and measuring the rate of decomposition of this reagent. J. W. Watson[91] questioned the mechanism of decomposition. A more fundamental criticism is that free radical acceptor ability, or number of active sites to which free radicals become attached, is not necessarily related to the rate of decomposition. Unless the mechanism of the decomposition is firmly established and shown to be dependent upon free radical acceptor ability, it would be extremely hazardous to try to measure active sites in this way. Lacking such information, it might be just as reasonable to view the results as indicating electron donor properties of the carbons. In our hands[92] the rate of persulfate decomposition and even the relative influence of different types of carbon black are very sensitive to the conditions under which the decomposition is conducted.

Garten and Sutherland also determined active sites by measuring the amount of a "benzidine blue" reagent which reacts irreversibly with the surface. This very unstable reagent is prepared by stepwise oxidation of a saturated solution of benzidine in 0.5% acetic acid with 0.005 *N* potassium permanganate. Although this reagent appears to be more satisfactory for measuring a kind of free radical acceptor ability, there are so many uncertainties in its use that a much more detailed study of it should be available before its utility can be evaluated.

Szwarc[93] has developed a technique for measuring the free methyl radical affinities of various pure compounds. Szwarc's results are generally reported in terms of relative methyl affinities with the methyl affinity of benzene taken as 1. If a series of polycondensed aromatic hydrocarbons are compared in this way, it is observed that the methyl affinities increase very rapidly with the number of rings in the compound. The logarithm of the methyl affinity varies inversely with theoretical values of the energy required to localize a π electron in these aromatic hydrocarbons. It increases with increasing values of free valency. All of this is in accord with the concept that, for polycondensed aromatic compounds, the larger the molecule, the more nearly its aromatic double bonds tend to react like aliphatic double bonds.

Szwarc[94] suggested that useful information would be obtained by measuring the free methyl affinities of various types of carbon black. The fact that carbon black decomposes peroxides makes the problem somewhat more difficult but, according to Szwarc[95], not impossible.

Since quinones are known to be powerful free radical acceptors, and since carbon black contains oxygen which appears to react like 1,4-quinone groups, one would expect that carbon black would possess pronounced free radical affinity from two sources: (1) its content of quniones, or quinone-like groups and (2) its resemblance to very large polycyclic aromatic hydrocarbons. It would, in fact, be very remarkable if carbon blacks did not show pronounced free radical activity. Although this free radical affinity seems to be of importance in determining the ability of carbon black to firmly bind rubber on its surface, we would expect that its effects on the reactions which take place during vulcanization might be of equal importance, cf. Section V.

9. The affinity of carbon black for some hydrogen containing materials.—Carbon black displays a pronounced affinity for a number of types of molecules which contain hydrogen. Some of these have been mentioned earlier in this section. A dramatic example of this affinity can be found in experiments[76] in which carbon black is exposed to a stream of wet air or wet nitrogen for a period of time at 65° C. If the sample so treated is dried in dry nitrogen at 150° C and analyzed for carbon, hydrogen, ash, etc., it will be found that its hydrogen content has increased considerably but that its oxygen content is virtually unchanged. (Philblack O treated in wet air for 32 days at 65° C, dried and analyzed as above, had a hydrogen content of 0.46% and an oxygen content of 0.56%. The untreated sample analyzed 0.31% hydrogen and 0.62% oxygen.)

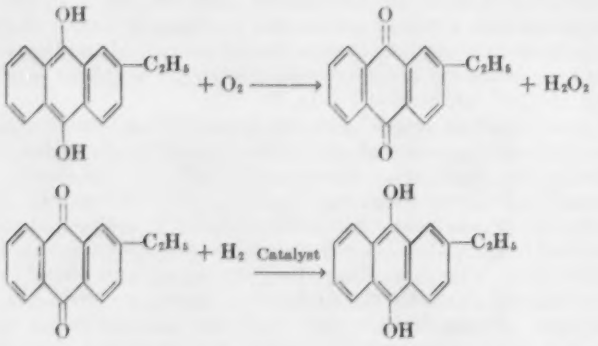
The carbon black apparently chemisorbs the water molecules with dissociation and preferential retention of one of the dissociation products. In the dynamic treatment, e.g., in the absence of the products of reaction, the carbon black preferentially retains hydrogen. (In static experiments, the change in hydrogen content was negligible (0.01 to 0.02%); the effect on oxygen content was questionable.) This affinity for moisture is tremendous. Carbon black will remove moisture under the conditions described above from air or nitrogen which has been dried successively by sulfuric acid, magnesium perchlorate and phosphorus pentoxide.

It is tempting to speculate that similar chemisorption of rubber molecules with dissociation into a rubber radical and a neutral hydrogen atom and subsequent chemical combination between the rubber radical and the carbon black particle is responsible for the irreversible adsorption of rubber as observed by Kraus and Dugon[51] (cf. Section IV, D, 7).

10. The activation of oxygen by carbon black.—It has been known for many years that the oxidizing power of oxygen is enhanced by adsorption on charcoal, a near relative of carbon black. Lamb and Elder[96] state that this was known by De Saussure[96] in 1815 and Stenhouse[96] in 1854. Calvert[96] in 1867 showed that oxygen adsorbed on charcoal oxidizes ethyl alcohol to acetic acid and ethylene to carbon dioxide and water. Many observations of this nature are to be found in the literature. The interesting study by Lamb and Elder[96] shows how effectively charcoal promotes the oxidation of ferrous to ferric ions by atmospheric oxygen. Atmospheric oxygen produces this conversion very slowly unless some type of "promotor" or catalyst is present, but charcoal in acidic solutions increased the rate of oxidation several hundred times. Lamb and Elder state, "The outstanding fact established by our experiments is that the very substances, namely charcoal, platinum and cupric salts, which hasten markedly the decomposition of hydrogen peroxide, particularly in the presence of ferrous salt solution, also greatly accelerate the oxidation of ferrous salt solutions by gaseous oxygen. This parallelism at once suggests that the two phenomena may be intimately related". They then demonstrated that a material could be extracted from commercial charcoal with 1 *M* sulfuric acid which would liberate iodine from acidic iodide solution. After extraction with acid, no further test for peroxide was observed unless the sample was aerated. The "peroxide" was reformed by aeration. The quantities of "peroxide" were quite small, ca. 0.0001 equivalent of active oxygen per gram of charcoal. Values in this general order of magnitude can be found on reinforcing carbon blacks[97]. This would represent only a very small proportion of the total oxygen which is found by ultimate analyses.

Schwob and his collaborators[98,99] studied this same general phenomenon by studying the oxidation of uracil and the formation of indophenol by the atmospheric oxidation of a mixture of α-naphthol and p-phenylenediamine. In these and other reactions, charcoal displays a definite catalytic influence; it activates oxygen. These phenomena are accompanied by electrochemical effects. It is suggested that similar phenomena may be of importance in the oxidation of vulcanized rubber containing carbon black[100,101]. It would be interesting to see what a professional electrochemist could do with these reactions. Potentially the experiments that can be conducted in aqueous solutions are susceptible to interpretation, but the electrochemistry of a filled vulcanizate would surely frighten the theoretical electrochemist. We might, however, be able to reason by analogy from the data obtained in the two systems and obtain tentative conclusions which would be useful in attempting to explain the behavior of various fillers. In addition, it would be worthwhile to try to demonstrate the presence or absence of hydrogen peroxide in a filled vulcanizate during oxidation.

One might speculate that the formation of hydrogen peroxide in rubber-containing carbon black might involve the quinone (or hydroquinone in its reduced state) structure of the carbons somewhat analogous to the formation of hydrogen peroxide by autoxidation of quinones[102], which has been employed commerically. The hydrogen for the reduction coming from the α-methylene



hydrogen of the rubber molecules, leaving a radical which would be a likely point of attack by oxygen molecules or by radicals formed from the decomposition of hydrogen peroxide.

The similarity in chemical behavior between oxygen and sulfur might lead us to wonder if this catalytic activity of carbon in promoting oxidation might not be related in some way to its activity in promoting dehydrogenation of rubber by sulfur, apparently an important step in vulcanization.

V. CHEMICAL EFFECTS OF CARBON BLACK DURING VULCANIZATION

A. INTRODUCTION

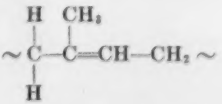
Although the function of carbon black in rubber is far from that of an inert filler, our knowledge of the process of reinforcement is fragmentary, at best. Considerable argument has taken place as to whether the action of carbon black

in rubber is a chemical one or whether it is purely a physical phenomenon. Comparatively few data have been available to aid in the choice between the two schools of thought. On the one hand, many investigators have felt that an action as pronounced as that of carbon black on an SBR type rubber, for example, involved a contribution by forces which were at least comparable in magnitude to those involved in vulcanization itself. On the other hand, colloid chemists have frequently approached the problem by drawing analogies between rubber-filler mixtures and pigment-vehicle systems such as putty or highly loaded paints. Certain physical forces have been used to explain the properties of such systems. These forces are quite real, but calculations of their magnitude[103] indicate that they would not be expected to account for the phenomenon of reinforcement.

The material presented in this section stems from an effort to determine whether any evidence could be obtained which would point to chemical effects which can be associated with reinforcement of rubber by carbon black. As the work progressed, it became evident that the entire chemistry of vulcanization can be altered by the presence of carbon black in a compound. Others have come to essentially the same conclusion, namely that one of the most important effects of carbon black in vulcanized rubber is its influence on the reactions which take place during vulcanization. These include Blanchard[3], Kraus[7], Watson[91] and others.

B. VULCANIZATION

In this study, it is necessary to draw upon the work of others in the field of the chemistry of vulcanization. Such work is largely, but not completely, based upon studies of vulcanization using model systems and has been successfully pursued by the late E. H. Farmer and his associates at the British Rubber Producers' Research Association in England[104]. Others have also made excellent studies of the chemistry of vulcanization using model systems, notably Armstrong, Little and Doak[105], and Hull, Olsen and France[106]. Farmer[107,108] pointed out that, although olefins of the type



are highly reactive at the double bond, in many reactions the reactivity of the α-methylene hydrogen atoms is even more important. Sulfur is mainly used in organic chemistry as a dehydrogenating agent. This dehydrogenation is accelerated by amines and sulfides[109,110]. From the considerations of reactivity by Farmers and others we would expect sulfur to attack the α-methylene hydrogen atoms. A simple scheme leading to crosslinking might involve dehydrogenation with concomitant addition of sulfur as a diradical to the denuded α-methylene carbon atom, followed by attack upon another α-methylene hydrogen atom in an adjacent rubber molecule, or addition of the radical to a double bond in an adjacent rubber molecule.

Reactions directly involving the double bond which would lead to crosslinking are also possible, for instance, addition of hydrogen sulfide to the double bond, forming a thiol intermediate. This could add to the double bond of another rubber molecule or couple with like thiol intermediates on adjacent rubber

molecules. However, it seems likely that these reactions involving the double bond would be more susceptible to side reactions like cyclic sulfide formation which would compete with the crosslinking process for sulfur and, hence, result in less efficient use of the sulfur in crosslinking. One very important function of any compounding ingredient would be the direction of the competing chemical reactions towards those which are efficient in producing crosslinks from the vulcanizing agents.

According to this particular sketchy picture of vulcanization, any compounding ingredient would increase the amount of crosslinks formed if it promotes dehydrogenation, or if it promotes coupling of the dehydrogenated molecules which at this stage contain reactive groups like —SH or —S· in place of one of the α-methylene hydrogen atoms. In addition, crosslinking efficiency in sulfur cures would be promoted by any ingredient which promotes the formation of mono- or disulfides at the expense of polysulfides, or alternately which converts any polysulfide once formed to mono- or disulfide with liberation of the sulfur in active form. At the same time, the compounding ingredient should avoid, or at least not promote, undesirable side reactions like scission of carbon-to-carbon bonds in the rubber skeleton or cyclic sulfide formation.

Carbon black and zinc compounds appear to function in one or more of these ways.

Carbon black which is removed from heated model systems containing vulcanizing ingredients[77] and from vulcanized rubber, itself, contains considerable amounts of sulfur, nitrogen and zinc. This fact, and other considerations, point to a high level of chemical activity on the carbon black surface or in its immediate vicinity.

C. AN EXAMINATION OF SOME FUNCTIONS OF CARBON BLACK DURING VULCANIZATION

As we turn to the literature for clues as to just how carbon black can enter into or catalytically influence the reactions which take place during vulcanization, we find a few helpful papers. Hauser and Brown[111] first and, in more detail, Bloomfield[112,113] studied the change in unsaturation of natural rubber gum stocks during vulcanization. Bloomfield's results on simple rubber-sulfur mixtures show that one double bond is lost for each sulfur atom which combines during cure. This loss in unsaturation per sulfur atom combined was reduced about 20% by the addition of the accelerator, MBT, activated with zinc oxide and stearic acid. Figure 22 presents a plot of Bloomfield's data from Table III of Reference 113.

Even before Bloomfield's work, Thornhill and Smith[114] published data for gum stocks which are in general agreement with his. Similar results were found with the same base compounds to which clay was added. However, a surprising result was found when a channel black was incorporated into an MBT-accelerated compound: *no loss in unsaturation was found with increasing amounts of combined sulfur.* When the German carbon black, CK-3 was used, the reduction in unsaturation was very slight, Figures 23 through 27. Thornhill and Smith's results were confirmed in substance by Bergem[115].

Unfortunately, the procedures for determining unsaturation in vulcanized stocks leave much to be desired. The oxidative degradation to which the stocks are subjected to make them soluble might very well be described as an analyst's nightmare. However, for whatever they are worth, they certainly suggest a possible important action of carbon black during vulcanization.

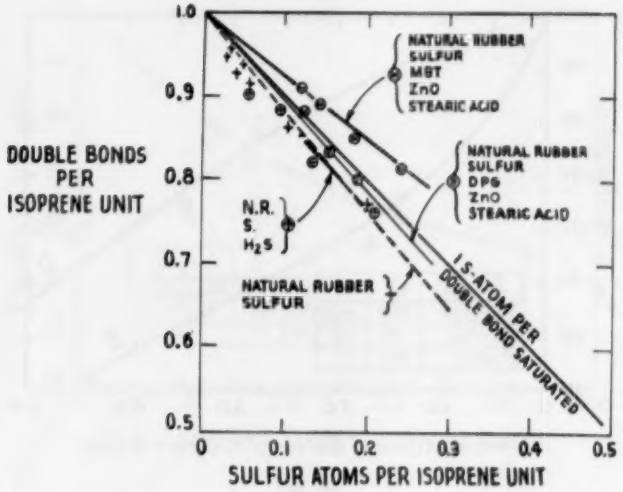


FIG. 22.—The decrease in unsaturation of natural rubber as a function of combined sulfur for several rubber compounds.

Recently Kraus[7] published work which indicates that the SAF black, Philblack E, markedly reduces the number of combined sulfur atoms per crosslink formed in sulfur-cured, Santocure-accelerated, cold rubber stocks. Data from Table VIII of Kraus's paper are listed in Table XII. The conclusion that the carbon black has increased the crosslinking efficiency of the vulcanizing agent is almost inescapable.

Accelerator requirements for channel black-loaded stocks are generally considered to be greater than for stocks which contain furnace blacks. The

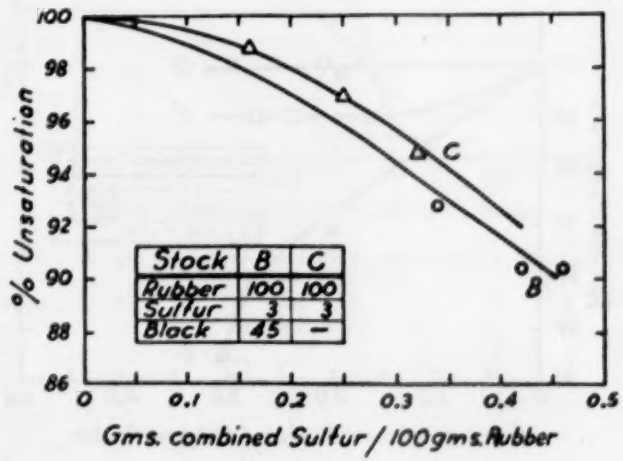


FIG. 23.

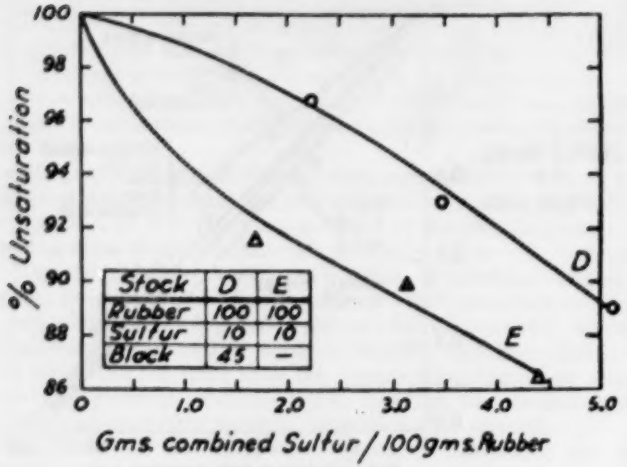


FIG. 24.

difference is especially pronounced with basic accelerators. This has been attributed to "adsorption" of the accelerator by the carbon black, and the familiar DPG test has been used for many years to evaluate curing rate and/or accelerator requirements of various carbon blacks[116,117].

Carbon black has been shown to have a high affinity for mercaptobenzothiazole or its reaction products. The nitrogen contents of the carbon blacks removed by extended extraction from model systems based on squalene represent quite appreciable portions of the nitrogen added to the systems as accelerator[77]. We shall discuss this further in Section V, E.

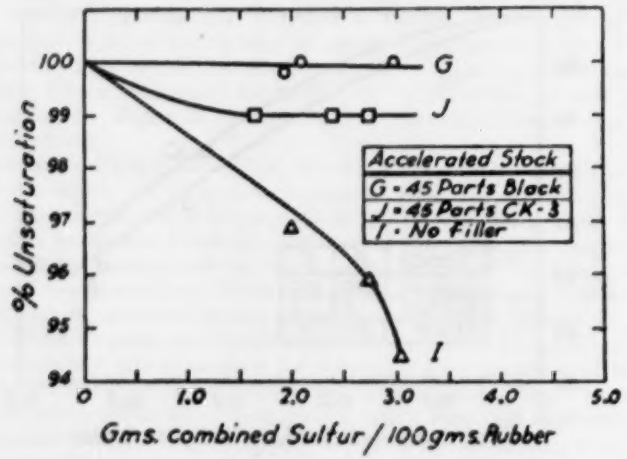


FIG. 25.

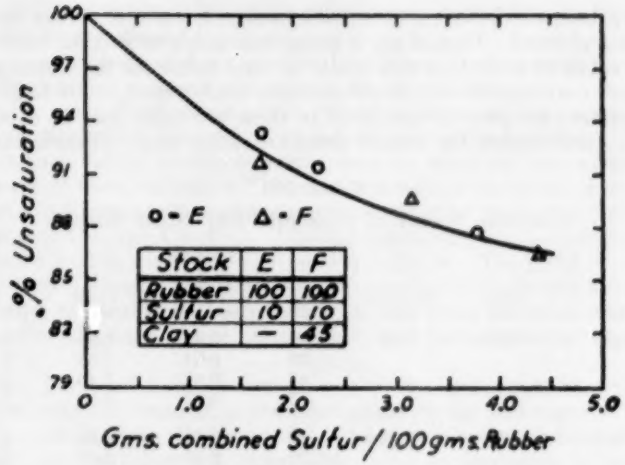
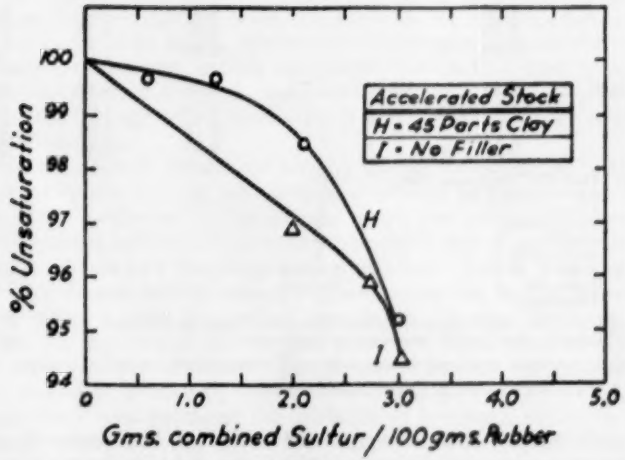


FIG. 26.



FIGS. 23 to 27.—The changes in unsaturation and combined sulfur of natural rubber stocks during vulcanisation

Compound	B	C	D	E	F	G	H	I	J
Pale crepe	100	100	100	100	100	100	100	100	100
Zinc oxide	—	—	—	—	—	5	5	5	5
Sulfur	3	3	10	10	10	3	3	3	3
Pine tar	—	—	—	—	—	3	3	3	3
MBT	—	—	—	—	—	0.9	0.9	0.9	0.9
Stearic acid	—	—	—	—	—	4	4	4	4
Agerite-Hipar	—	—	—	—	—	1	1	1	1
Filler									
Channel black	45	—	45	—	—	45	—	—	—
Kaolin	—	—	—	—	45	—	45	—	—
CK-3 black	—	—	—	—	—	—	—	—	45

What, then, are the logical chemical functions required of carbon black to fit into such a picture? First of all, it seems reasonable to look for some type or types of catalytic activity which would be responsible for the chemical effects which have been described. In the normally loaded stock, quite large areas of carbon surface are present compared to those normally used in catalytic reactions. Furthermore, the contact times are rather long. If carbon black has

TABLE XII

COMBINED SULFUR IN COLD SBR–SAF BLACK-STOCKS

Stock[1]	Sulfur, phr	Santocure, phr	Cure time, min	Fraction of total sulfur combined[2]	$\nu \times 10^4$ moles/cc	$(S)/\nu^3$
Gum	1.75	1.25	20	0.89	1.20	3.8
			30	0.94	1.39	3.4
			45	0.97	1.40	3.6
			75	0.97	1.38	3.6
Black	1.75	1.25	10	0.73	0.88	4.3
			20	0.83	1.68	2.5
			30	0.91	1.89	2.5
			45	0.89	1.91	2.4
			75	0.78	1.94	2.1
Gum	1.25	1.25	75	0.95	0.99	3.5
	1.50			0.95	1.21	3.4
	1.75			0.97	1.38	3.6
	2.25			0.98	1.77	3.6
Black	1.25	1.25	75	0.88	1.40	2.3
	1.50			0.79	1.67	2.1
	1.75			0.78	1.94	2.1
	2.25			0.97	2.48	2.6

[1] Recipe:

Cold SBR (Philprene 1500)	100
SAF (Philblack E)	42
Circosol 2 × H	2
Paraflux 2016	2
Zinc Oxide	3
Stearic Acid	2
Sulfur	Variable
Santocure	Variable
Flexamine	1

[2] Calculated from free sulfur analyses, method of Oldham, Baker and Craytor.
[3] (S) = Combined sulfur in gram atoms per cc of polymer.

ν = Effective number of network chains $= 2n - \frac{2\rho}{M}$ where n is the number of crosslinks, ρ is the density and M is the primary molecular weight of the polymer.

any catalytic activity whatsoever, these two factors, large areas of surface involved and the comparatively long contact times, would make possible catalytic effects worthy of our consideration.

If attack by sulfur radicals or sulfur-containing radicals upon the α-methylene hydrogen atoms is an important initial step in vulcanization, we might ask whether carbon black is able to function during vulcanization as a dehydrogenation catalyst. Various types of carbon, including carbon black, have been shown to behave as mild dehydrogenation catalysts; but the temperatures empolyed are generally several hundred degrees above vulcanization temperatures. (See however, Reference 88 where a small amount of dehydrogenation of decalin was observed in presence of charcoal at 90° C.) We will examine this function of carbon black in the next section of this paper, where it will be shown

that carbon black is a catalyst in the dehydrogenation of tetralin by sulfur at vulcanizing temperatures.

If carbon black promotes removal of hydrogen from α-methylene carbon atoms, the denuded molecule will contain an active, radical site. In the mixtures used to bring about vulcanization of rubber, there are many sources of free radicals, particularly sulfur-containing radicals and sulfur diradicals. (Radical formation from sulfur, accelerators, etc., may be catalyzed by carbon black.) Surely some of these radicals will react at the radical site which is created by removing a hydrogen atom from an α-methylene carbon atom, but the resulting materials may then react further. One end result would be coupling of rubber molecules by sulfide, disulfide or polysulfide linkages. The point of attack on the second rubber molecule might be at the α-methylene hydrogen atom, at the double bond, at the denuded α-methylene carbon atom (a rubber-free radical) or at a sulfur atom attached to the α-methylene carbon atom or at a double bond.

Farmer, Ford and Lyons[118] have shown quite convincingly that zinc compounds promote self-coupling of the alkenylthio groups and suppress addition of such groups in olefin double bonds. It is possible that carbon black acts similarly. Such coupling can conceivably result in formation of sulfide, disulfide or polysulfide linkages.

Any catalyst which would decompose polysulfide linkages would be expected to release sulfur in active form from any polysulfide groups present in the vulcanizate or prevent polysulfide formation. In either case, sulfur, which would otherwise go into polysulfides, would be available for crosslink formation. It may be significant that, in the production of hydrogen polysulfides (sulfanes) by an electrolytic process, carbon electrodes could not be used because they cause decomposition of the H_2S_n compounds[119]. This, then, may be another catalytic effect through which carbon black increases the number of crosslinks during vulcanization.

Hydrogen sulfide is invariably formed during vulcanization with sulfur. The amounts appear to vary considerably according to the accelerators[113] and probably other compounding ingredients which are present. Carbon black promotes hydrogen sulfide formation catalytically[120], which probably is directly related to its action as a dehydrogenation catalyst. Unless taken up as zinc sulfide, the hydrogen sulfide formed can add to double bonds, forming mercaptans by either a polar or a radical mechanism. Barton, however, has observed that the presence of mercaptans could not be demonstrated in cured rubber[121]. Presumably, if formed, they couple so rapidly with similar groups that they should be considered only as intermediates.

Carbon black also promotes the oxidation of hydrogen sulfide to sulfur[120]. By analogy, we might expect carbon black to promote the oxidative coupling of mercaptan intermediates by sulfur. If carbon black decomposes polysulfide bonds, and if it promotes coupling of mercaptans or other intermediates, then such coupling would likely result in disufide linkages as the end product.

Carbon black promotes the breaking of —O—O— and quite possibly —S—S— bonds. This was just mentioned in connection with polysulfide crosslinks. However, at least of equal importance in many, if not all, stocks would be the significance of such action on activating accelerators of vulcanization and in some cases, at least, actual vulcanizing agents. This will be discussed further in Section V, D. *Thus, the whole chemistry of vulcanization may be altered by carbon black.*

Adsorption of rubber molecules and/or curing agents may result in orienta-

tion of the molecules so that potentially reactive sites are present in favorable positions for crosslinking. Furthermore, the chemisorption of rubber molecules may result in partial or complete dissociation of α-methylene hydrogen atoms, and this would tend to direct the action of reactive radicals at the α-methylene carbon atom.

It is possible to speculate on other catalytic and chemical actions of carbon black which might be important in reinforcement of rubber, but these would take us too far afield to be justified at this writing.

1. Carbon black as a catalyst for dehydrogenation by sulfur.—Carbon black has been described as a mild dehydrogenation catalyst in contrast to the more severe dehydrogenation catalysts. These more severe catalysts, like silica-alumina, not only promote dehydrogenation but commonly also promote chain scission. Generally, dehydrogenation by carbon black alone is conducted at temperatures several hundred degrees above vulcanization temperatures. For instance, carbon black dehydrogenates[122] decalin at 520–550° C. Tetralin is more readily dehydrogenated than decalin.

If dehydrogenation of α-methylene hydrogen atoms is the initial step in the vulcanization of rubber by sulfur, it would be desirable to be able to study the influence of various commonly used compounding ingredients on this dehydrogenation step. Rubber, itself, is not a suitable molecule to start with in such an investigation because of its enormous molecular weight. Simpler molecules would seem more appropriate for such work. Tetralin has frequently been employed to study dehydrogenation by sulfur because it is readily dehydrogenated to naphthalene at temperatures of about 200° C or above. Accordingly, a study was made of the dehydrogenation of tetralin to naphthalene by sulfur in the presence of a number of compounding ingredients, including carbon black.

Mixtures of unpurified tetralin (Eastman) and various combinations of sulfur, accelerator, carbon black and zinc laurate were heated for one hour at 150° or 200° C in an atmosphere of nitrogen. The mixtures were then steam distilled and the per cent naphthalene was determined spectrophotometrically using the method of Mellon and Moss[123]. Since the original tetralin contained some naphthalene, 0.43%, this blank was deducted from the total naphthalene content of the mixture to give the increase in naphthalene content due to the treatment.

(1) The effect of sulfur on the dehydrogenation of tetralin is indicated by the following data:

Tetralin	100.	100.
Sulfur	—	3.00
Naphthalene (200°), %	-Blank-	0.70
Naphthalene (150°), %	-Blank-	0.34

(2) Philblack O, by itself, will not act as a dehydrogenating agent for tetralin at 200° C:

Tetralin	100.	100.0
Philblack O	—	50.
Naphthalene (200°), %	-Blank-	(−0.03)
Naphthalene (150°), %	-Blank-	0.04

(3) However, Philblack O acts as an effective catalyst for the dehydrogenation of tetralin by sulfur:

Tetralin	100.	100.
Philblack O	—	50.
Sulfur	3.00	3.00
Naphthalene (200°), %	0.70	1.43
Naphthalene (150°), %	0.34	0.44

(4) A similar effect on the dehydrogenation of tetralin is shown by Philblack O in the presence of the accelerator for vulcanization of rubber, mercaptobenzothiazole (MBT), activated with commercial zinc laurate (Laurex):

Tetralin	100.	100.
Philblack O	—	50.
Sulfur	3.00	3.00
MBT	1.00	1.00
Laurex	20.	20.
Naphthalene (200°), %	1.07	1.54
Naphthalene (150°), %	—	0.71

(5) As one would expect, MBT, activated by Laurex, promotes the dehydrogenating action of sulfur on tetralin:

Tetralin	100.	100.
Sulfur	3.00	3.00
MBT	—	1.00
Laurex	—	20.
Naphthalene (200°), %	0.70	1.07
Naphthalene (150°), %	0.34	—

(6) However, the accelerator, MBT, activated with Laurex, had but slight effect, if any, on the dehydrogenation of tetralin in the presence of carbon black:

Tetralin	100.	100.	100.
Philblack O	50.	50.	50.
Sulfur	3.00	3.00	3.00
MBT	—	1.00	1.00
Laurex	—	—	20.
Naphthalene (200°), %	1.43	1.57	1.54

In the presence of carbon black, the zinc laurate did not activate the accelerator, e.g., any activation was apparently furnished by the carbon black, and no enhancement of the dehydrogenating action of *carbon black, sulfur and MBT* was provided by the Laurex.

(7) Furthermore, although zinc compounds are normally mild dehydrogenation catalysts, the following results do not indicate that Laurex alone will dehydrogenate tetralin at 200° C. (At higher temperatures, some effect might be found.)

Tetralin	100.	100.
Laurex	—	20.
Naphthalene (200°), %	-Blank-	(−0.06)

(8) Addition of 20 parts Laurex, in the absence of accelerator, actually reduced the catalytic effect of Philblack O on dehydrogenation of tetralin by sulfur:

Tetralin	100.	100.
Philblack O	50.	50.
Sulfur	3.00	3.00
Laurex	—	20.
Naphthalene (200°), %	1.43	0.98

(9) Although some caution should be used in attempting to interpret these data in terms of what would be expected to take place in rubber, they certainly point to an important catalytic activity of carbon black. The data are significant in pointing to a function of carbon black which is not shared by zinc compounds. Dehydrogenation of rubber at the α-methylene carbon atoms is viewed here as an initial step in vulcanization. The mechanism by which carbon black promotes this action is not known. Amines and sulfides promote dehydrogenation of tetralin[109,110], apparently by opening S_8 rings. Perhaps this is also involved in the catalytic activity of carbon black, but if so it may be only one of several functions of the carbon black. Adsorption of rubber molecules with dissociation of hydrogen atoms could also be visualized. This, if it occurs, would be a mode of directing the action of sulfur at the α-methylene carbon atoms.

(10) What has been said should not be construed to mean that the action of carbon black as a catalyst for dehydrogenation of rubber by sulfur is its only, or even its chief, chemical function during vulcanization. The relative importance of this activity will be quite dependent upon the nature of the curing system. In some vulcanizing systems—for instance when a very strong dehydrogenating agent is involved, as in TMTD "sulfurless", cures—this activity of the carbon black may be of minor, or even no, importance. The action of carbon black on curing might even be undesirable, as when natural rubber is cured with benzoyl peroxide[124]. The fact that carbon black is such a useful compounding ingredient may be somewhat dependent upon the general use of sulfur cures.

2. The relationship between carbon black and polysulfides.—Dehydrogenation of rubber by sulfur during vulcanization is believed to be followed with or accompanied by a series of reactions, as yet not completely formulated, which lead to the coupling of molecules by —S—, —S—S— or —S—(S_x)—S— crosslinks. Other considerations remaining equal, the larger the number of sulfur atoms in one crosslink, the fewer crosslinks will be produced in the vulcanized network. If polysulfides are formed in a given vulcanizate, addition of any material which will decompose polysulfide linkages without entering into a permanent chemical combination with the liberated sulfur would make additional quantities of sulfur available for crosslink formation. At the present time, we do not have data showing that carbon black is such a material. However, several considerations indicate that this is quite possible.

As mentioned previously, in the formation of hydrogen polysulfides (sulfanes) by electrolytic reduction of sulfurous acid, carbon electrodes cannot be used because carbon decomposes the sulfanes[119].

Furthermore, there appears to be a marked similarity between those materials which decompose the hydrogen polysulfides[125] and those which decompose hydrogen peroxide. Carbons decompose hydrogen peroxide; the basic carbons are especially active. On the other hand, the various organic poly-

sulfides exhibit decided differences in stability[126]. It seems reasonable to expect carbon black to promote the decomposition of some organic polysulfides. Experimental data are needed to determine whether this possible function of carbon black is of importance during vulcanization.

3. The relationship between carbon black and hydrogen sulfide.—The problem of just how hydrogen sulfide and carbon black fit into the vulcanization reactions is much too complex for us to untangle now. Some observations might, however, be in order. Craig *et al.*[127] believe that hydrogen sulfide is necessary to activate TMTD and other accelerators of vulcanization (cf. Section V, F). Carbon black at 150° C has been shown to catalyze the formation of hydrogen sulfide[120]; this would seem to be largely if not solely a result of its action as a catalyst for dehydrogenation by sulfur.

As mentioned in Section IV, D, 3, carbon black reacts very readily with hydrogen sulfide at vulcanizing temperatures[75]. It was shown that the extent of this rapid reaction is directly proportional to the amount of hydrogen which reacts with carbon black at room temperature in the presence of the Adams (reduced platinum oxide) catalyst. It was further suggested that the carbon black contains 1,4-quinone groups[68] which are involved in both the rapid hydrogen sulfide reaction and the catalytic hydrogenation. If hydrogen sulfide reacts by 1,4 addition to a quinone structure in the carbon black, its level in the rubber compound will be reduced, at least initially. Furthermore, experiments have shown that the oxygen content of the carbon black appears to reduce the quantity of hydrogen sulfide formed[120]. Hence, the oxygen content of carbon black will act to inhibit, or at least retard, those steps in vulcanization which are dependent upon hydrogen sulfide. This may be one of the chief reasons that many channel black stocks are slower curing than furnace black stocks.

1,4 addition of hydrogen sulfide to carbon black would presumably produce thiol groups. These might then be expected to react by coupling to rubber molecules during vulcanization. However, the bond between carbon black and rubber is apparently strong enough—however it is formed—that these additional carbon black-sulfur-rubber linkages would be superfluous and actually wasteful of sulfur because it could not take part in ruber-to-rubber crosslinking.

Carbon black catalyzes the oxidation of hydrogen sulfide to sulfur by atmospheric oxygen[120]. If oxidizing agents are present which could perform this conversion, then the oxidation of hydrogen sulfide to sulfur which could participate in vulcanization would be catalyzed by carbon black. It is not known whether this is of any importance in the vulcanization of practical rubber compounds, but it could be.

We will return to this topic again in Section V, F where the action of zinc compounds in vulcanization will be discussed.

D. CATALYSIS OF DECOMPOSITION OF —O—O— AND —S—S— BONDS

In section V, C, 2, it was observed that carbon black might be expected to destroy some of the less stable polysulfide bonds. This leads to a consideration of possible catalytic action on several related types of molecules. We shall consider hydrogen peroxide, benzoyl peroxide and tetramethylthiuram disulfide.

1. Hydrogen peroxide.—It has been known for some time that various forms of carbon, including carbon black, promote the hetrogeneous decomposition of hydrogen peroxide. The literature has been reviewed recently by Schumb, Satterfield and Wentworth[128]. Carbons which contain large amounts of oxygen

TABLE XIII

THE EFFECT OF BUFFER (pH = 7.0) ON THE DECOMPOSITION OF HYDROGEN PEROXIDE IN THE PRESENCE OF CARBON BLACK

Carbon black	pH of carbon black slurry[1]	Hydrogen peroxide decomposed as mg oxygen/g carbon[2]	
		Unbuffered	Buffered to pH of 7.0
Mogul (LFC)	2.8	0.64	11.4
Spheron 9 (EPC)	4.5	2.48	4.96
Philblack E (SAF)	9.5	15.4	9.2
Philblack O (HAF)	9.3	7.4	4.9

[1] pH as determined in distilled water.
[2] 0.250 g carbon black added to 15 ml of approx. 0.37 N H_2O_2, stirred for 2 hours at 25 ± 1° C. Hydrogen peroxide decomposition determined by permanganate titration.

and whose slurries show an acid pH are less effective in promoting hydrogen peroxide decompositon than those whose slurries are basic. Buffering the solutions to a pH of 7.0 reduced the activity of the basic carbons and promoted that of the acidic carbons. Table XIII shows this effect for four typical carbon blacks whose primary properties are listed in Table II.

The action of carbon black in promoting the decomposition of hydrogen peroxide was studied at room temperature in solutions buffered to a pH of 7.0. The total hydrogen peroxide decomposition was obtained by titration with permanganate. It was found that the rate of decomposition is very nearly proportional to the surface area of the carbon black and inversely proportional to its hydrogen content, Figure 28. Wetting difficulties prevent the use of acetylene black in this work and may contribute to the scattering of the points in the cases of Philblack A and Philblack O.

In general, the decomposition of hydrogen peroxide is promoted by electron donors. Very extensive studies have been conducted upon the decomposition of hydrogen peroxide by ferrous ions. The initiation of decomposition, according to the presently accepted Haber and Weiss mechanism[129], involves the

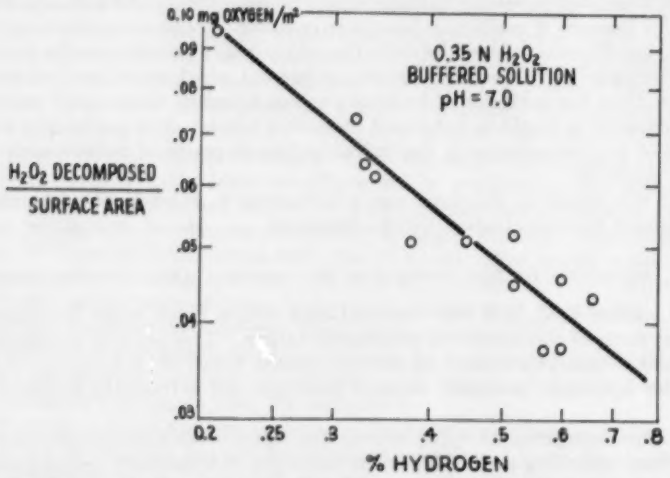


FIG. 28.—The decomposition of hydrogen peroxide buffered to a pH of 7.0 by various carbon blacks is mainly dependent upon their surface areas and hydrogen contents.

transfer of an electron to the hydrogen peroxide:

$$(1)\quad Fe^{++} + H_2O_2 \rightarrow Fe^{+++} + \cdot OH + OH^-$$

From this point on, the reaction[123], according to Barb, Baxendale, George and Hargrave, proceeds according to the following reactions:

$$(2)\quad Fe^{++} + \cdot OH \rightarrow Fe^{+++} + OH^-$$

$$(3)\quad H_2O_2 + \cdot OH \rightarrow \cdot O_2H + H_2O$$

$$(4)\quad Fe^{++} + \cdot O_2H \rightarrow Fe^{+++} + HO_2^-$$

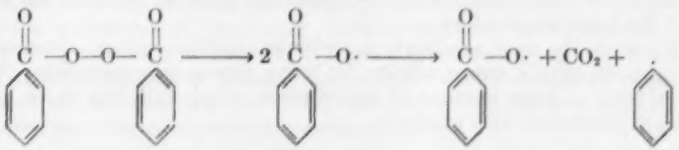
$$(5)\quad Fe^{+++} + \cdot OH_2 \rightarrow Fe^{++} + H^+ + O_2$$

The important reaction here is the initiation reaction, (1). If carbon black can denote electrons to the hydrogen peroxide molecule, it could act like the ferrous ion in promoting the decomposition. Foreign atoms, other than carbon, would tie up electrons and reduce the ability of the carbon black to act as an electron donor.

2. Benzoyl peroxide.—Carbon black also promotes the decomposition of benzoyl peroxide, as shown by Braden, Fletcher and McSweeney[124]. Their procedure shows considerable differences between various kinds of carbon black.

The chemistry of benzoyl peroxide decomposition has been extensively studied. An excellent review was published recently[130]. The nature of the products is dependent upon the environment; solvent effects, inhibitors and promotors have been observed. The action of carbon black in promoting the decomposition of benzyol peroxide has not been elucidated. In view of the pronounced tendency for it to decompose homogeneously into radicals, the mechanism by which carbon black promotes its decomposition may be different from that for hydrogen peroxide. On the other hand, an initiation step similar to that for hydrogen peroxide could be involved. In general, the products of decomposition of benzoyl peroxide can be considered to be two benzoyl radicals, one of which can decompose further to give a phenyl radical and carbon dioxide.

Either the benzoyl radicals or the phenyl radicals can attack the solvent or various radical acceptors which may be present. The overall reaction can be visualized as being:



in which the ratio of benzoyl radicals to phenyl radicals will be determined by the environment of the decomposition, for instance, the presence or absence of radical acceptors. One contribution of carbon black to the decomposition of benzoyl peroxide may be to influence that environment. In the nonpolar solvent, toluene, benzoyl peroxide decomposition at room temperature was found to be proportional to the carbon black surface within the probable experimental error[92].

3. Tetramethylthiuram disulfide.—The similarity in the structure of benzoyl peroxide and TMTD was pointed out by Farmer[131]. TMTD (sulfurless) cured stocks containing carbon black are more scorchy than unloaded stocks. However, the relative effect of different types of carbon black seems to be somewhat dependent upon the content of zinc. With 3.00 parts Laurex (commercial zinc laurate), the scorchiness seems to be directly related to the surface area of the carbon black. The important feature, however, is that all carbons tested markedly reduced scorch times. This, together with the similarity in structure of TMTD and benzoyl peroxide, suggests that carbon black makes a stock more scorchy by promoting the decomposition of TMTD. Experiments to prove this hypothesis should not be too difficult.

4. Polysulfide intermediates.—It has been suggested[132] that at least some accelerators react to open sulfur rings and that unstable polysulfides of the type R—S—(S)$_x$—S—R are formed which can decompose to furnish sulfur radicals or diradicals which are active in vulcanization.

Dogadkin and Tutorskii[133], according to the abstract in *Chemical Abstracts*, report that such polysulfides can be isolated in which two mercapatobenzothiazole end groups are connected by a chain of five sulfur atoms. If carbons are able to decompose polysulfide chains, they would presumably either prevent such molecules from forming or, if formed, readily decompose them with the liberation of sulfur radicals or diradicals which would then enter into the vulcanization reactions. This is one of several possible ways by which carbon black may activate vulcanization.

E. NOTES ON THE REMOVAL OF ACCELERATOR BY CARBON BLACK

During the 1920's and 1930's, channel black was the commonly used reinforcing black, and many rubber stocks containing it were compounded using the basic accelerator, diphenylguanidine (DPG). It was found that there was a general inverse relationship between the curing rate of such stocks and the volatile content of the channel black. This was explained as being due to accelerator adsorption, the adsorption of the basic accelerator being attributed mainly to acidic oxygen-containing groups on the surface of the channel black. With the carbons then generally used, this was a very useful concept, and the familiar DPG adsorption test was used both for control testing at the carbon black plants and as a specification test by the rubber companies.

It was known that other accelerators were adsorbed, like the acidic MBT, but the extent of such adsorption was considered to be far less than the adsorption of the basic accelerators.

All commonly used accelerators for vulcanization contain nitrogen, and carbon blacks have a strong affinity for many nitrogenous materials. This is evident from a large number of experiments which fall into three groups. These are illustrated with examples.

(1) The increase in nitrogen content of carbon black when treated with dimethylamine was described in Section IV, D, 5.

(2) The affinity of carbon black for the nitrogenous materials in natural rubber was discussed in Section IV, D, 6.

(3) Carbon blacks removed from natural rubber vulcanizates by oxidative degradation procedures like that described in Section IV, D, 6 contained considerable amounts of nitrogen. Values as high as 1.11% nitrogen have been found for carbon black which was removed from TMTD (sulfurless) cures

formulated from smoked sheets, 100; carbon black (Elf O), 50; TMTD, 3.50; and Laurex, 3.00.

Likewise, carbon blacks removed by prolonged extraction from model systems containing MBT as the accelerator always contained a material portion of the nitrogen added as accelerator[77].

In some cases, interesting stoichiometric relations can be worked out from the data, such as that shown in the next section, but the subject is too complex to deal with exhaustively.

The important feature is that the ratios of various atoms present in the original accelerator are sometimes considerably different from what they are when removed to the carbon black surface. Furthermore, the quantities involved are sufficiently large as to indicate considerable activity at the carbon

TABLE XIV

EFFECT OF HYDROGEN SULFIDE CONCENTRATION ON GELLING OF NATURAL RUBBER CEMENTS [5]

Unloaded cements[1]				Philblack O cements[2]			
Ml H_2S	Sulfur (parts)[2]	Ml air	Relative viscosity	Ml H_2S	Sulfur (parts)	Ml air	Relative viscostiy[4]
0.5	—	—	0.85	0.5			1.4
1.0			1.2	2.0			1.6
1.5			1.55	4.0			6.6
2.0			Gelled	6.0			No. 2 Quality gel
2.5			Gelled	8.0			No. 1 Quality gel
3.0			Gelled	10.0			No. 3 Quality gel
4.0			1.6	8.0	1		No. 3 Quality gel
6.0			1.1	8.0	6		No. 1 Quality gel
8.0			1.0	8.0		2.0	No. 4 Quality soft, sticky gel
10.0			0.8				
2.0	1		Gelled				
0	2		1.1				
0	6		1.2				
2		1.5	About ½ gelled				

[1] Base cement: 400 g toluene; 40 g rubber compound (pale crepe, 100; TMTD, 4; zinc oxide, 5).
[2] Parts sulfur per 100 parts pale crepe in cement.
[3] 50 parts Philblack O per 100 parts pale crepe in cement.
[4] Gel quality: No. 1 firmest gel; No. 4 softest gel.
[5] 5 cc of each cement in serum bottles with rubber stopples evacuated and filled with pure nitrogen, three times, then heated 1 hour at 70° C.

black surface or in its immediate vicinity. We cannot be sure whether the accelerator or accelerator fragments which are concentrated there are active or inactive in vulcanization; each case probably will have to be examined separately. It is possible that removal of some accelerator fragments, for instance dimethylamino radicals or dimethylamine from TMTD, alters the vulcanization reactions by removing one of the products of the reaction and, thereby, promoting one of several possible reactions.

F. THE PROBLEM OF ZINC COMPOUNDS AND HYDROGEN SULFIDE

One of the chief unsolved mysteries of rubber compounding is the function of zinc in vulcanization[124]. Virtually all rubber compounds which are cured with sulfur, even so called "sulfurless" cures in which TMTD is the vulcanizing agent, contain zinc; but its function in the rubber compound is still not clear.

As mentioned in Section V, C, Farmer, Ford and Lyons[118] demonstrated that zinc compounds promote self-coupling of alkenylthiol groups and suppress

addition of such groups to olefin double bonds. Craig *et al.*[127,135] considered the function of zinc to be to control the hydrogen sulfide level during vulcanization. They felt that a small, but definite, quantity of hydrogen sulfide was required to activate the process; but a high concentration of hydrogen sulfide would completely inhibit vulcanization. To demonstrate these effects, Craig[127] vulcanized natural rubber cements at 60° C with TMTD. He showed that no vulcanization took place in the absence of hydrogen sulfide. When hydrogen sulfide was added in increasing amounts, the cements set to gels; but there was an optimum concentration above which the cements would not gel. In the absence of zinc, none of the cements gelled. We have repeated Craig's work, adding carbon black to some of the cements. In the cements without carbon black, our results are in complete agreement with Craig's. In the presence of carbon black, more hydrogen sulfide must be added to produce a gel than in its absence, Table XIV.

Krebs and Weber[136] reported that sulfide ions, in the presence or absence of amines open S_8 rings. Further, Jennen reported that these sulfide ions[109], as well as amines[110], promote dehydrogenation of tetralin by sulfur. These observations are of obvious importance in the consideration of the action of hydrogen sulfide and accelerators[127] during vulcanization.

Bloomfield[113] conducted vulcanization experiments on simple rubber-sulfur mixtures *in vacuo* and concluded that hydrogen sulfide catalyzed the combination of sulfur with rubber in these simple mixtures. Zinc oxide partially suppressed this catalytic action, presumably by removing the hydrogen sulfide as zinc sulfide. Mercaptobenzothiazole and diphenylguanidine are stated to inhibit the catalysis entirely. Booth and Beaver[128], operating at high hydrogen sulfide concentrations, concluded that hydrogen sulfide inhibited rather than catalyzed vulcanization. Perhaps, as Craig[127] has indicated, the concentration of hydrogen sulfide is rather critical; and the results obtained depend mainly upon the concentration at which the various investigators were working.

We should like to point out that most fundamental investigations of the type referred to above are conducted on mixtures which do not contain carbon black. If carbon black is present, the relationships may be altered. For instance, Table XV lists stress-strain results on some very simple mixtures which contain carbon black. The samples were heated for one hour at 150° C in a vacuum oven or in hydrogen sulfide at atmospheric pressure and compared with the unheated samples. There is a small, but definite, indication that some curing is taking place—it can be best judged by hand tests. And yet, hydrogen sulfide in high concentrations is reported to inhibit cure and, at somewhat higher temperatures, to result in devulcanization. Surely, here the presence of carbon black has altered some feature of the rubber or of the rubber-accelerator-hydrogen sulfide system with respect to vulcanization. Incidentally, these results have been confirmed with quite a variety of mixtures, but including the complete data would neither significantly add to nor alter the picture. Channel black, which reacts more extensively with hydrogen sulfide, seems to show greater tendency to cure in this gas.

Let us examine the relationship between soluble zinc and carbon black a little further. When carbon black (50 parts) is heated for one hour at 150° C with squalene (100) and Laurex (20) and extracted for 30 days with chloroform in which both the squalene and zinc laurate are soluble, a definite zinc content is found for all the carbon blacks tested. This zinc content appears to be more nearly related to the active hydrogen found by the Zerewitenoff (Grignard reagent) method than to any other property of the carbons which we have

TABLE XV

CURING OF NATURAL RUBBER–CARBON BLACK MIXTURES WITH HYDROGEN SULFIDE

	Unheated			Heated 1 hour in vacuum oven @ 150° C			Heated 1 hour in H_2S @ 150° C			Heated 6 hours in H_2S @ 150° C		
Natural rubber	100	100	100	100	100	100	100	100	100	100	100	100
Philblack O	50	50	—	50	50	—	50	50	—	50	50	—
Spheron 9	—	—	50	—	—	50	—	—	50	—	—	50
MBT	—	1	1	—	1	1	—	1	1	—	1	1
Zinc oxide	—	5	5	—	5	5	—	5	5	—	5	5
Stearic acid	—	3	3	—	3	3	—	3	3	—	3	3
300% modulus (psi)	470	290	180	350	420	260	480	400	460	440	340	460
Tensile strength (psi)	710	400	190	400	440	300	830	560	890	680	880	850
% elongation @ break	340	370	310	330	310	320	440	350	420	410	460	430

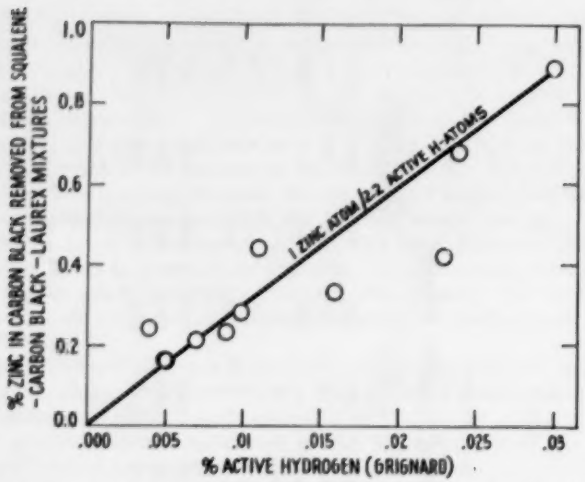


FIG. 29.—The amounts of zinc removed by various carbon blacks from heated solutions of zinc laurate in squalene are dependent upon their active hydrogen contents.

tested. For this mixture and this treatment, roughly one zinc atom was found for every 2.2 active hydrogen atoms, Figure 29. Perhaps only part of the groups containing active hydrogen are able to combine with the soluble zinc in these mixtures. (Extraction with glacial acetic acid removed 99% or more of the zinc content of these samples.)

Now, if we add MBT and sulfur to the above mixture and treat as before, we find a further increase in the amount of zinc in the samples[77]; but, in addition, the nitrogen and the sulfur contents of the samples are increased. The zinc in the extracted samples seems to be related in some way to the accelerator or accelerator fragments and the sulfur which combines with the carbon black.

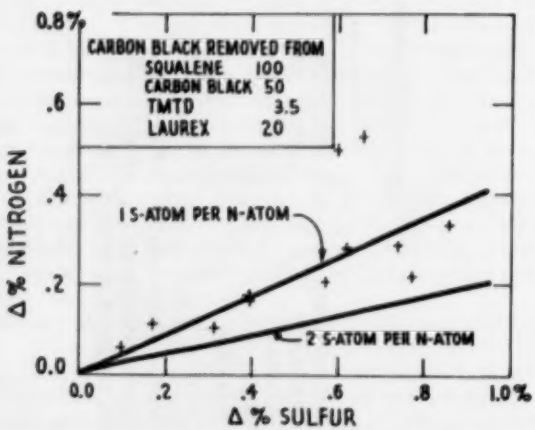


FIG. 30.—The increases in nitrogen and sulfur contents of various carbon blacks removed from heated mixtures of squalene, carbon black, TMTD and zinc laurate.

Once again, almost all of the zinc content of the samples could be removed by extraction with glacial acetic acid.

Now, if we add TMTD (3.50 parts) to the mixture of squalene, carbon black and Laurex and treat as before, we find rather large increases in nitrogen and sulfur contents of the carbon black after prolonged extraction The zinc contents also increase. In most cases approximately one sulfur. atom is present on the carbon for each nitrogen atom, Figure 3.0 Furthermore, the nitrogen values correspond fairly closely to one nitrogen atom for each active hydrogen found on the original samples, Figure 31. During the

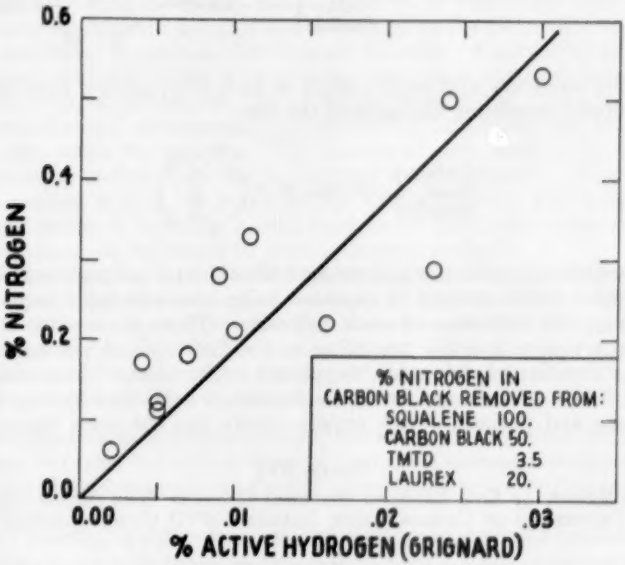


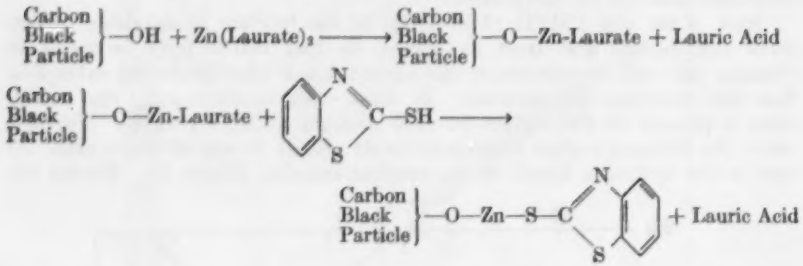
FIG. 31.—The increases in nitrogen contents of carbon blacks removed from heated mixtures of squalene, carbon black, TMTD and zinc laurate are roughly proportional to their active hydrogen contents.

heating, soluble zinc and TMTD and/or its decomposition products seem to be reacting at or near the carbon black surface. Squalene, too, is probably involved. Now, let us consider a few experiments with natural rubber.

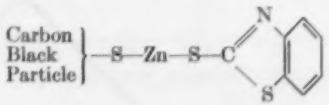
The literature contains statements to the effect that zinc is necessary in sulfurless cures with normal amounts of TMTD. (Craig[129] did obtain some cure without zinc in a stock prepared from 10 parts TMTD and 100 of rubber, but the 600% modulus was only 250 psi.) In the presence of carbon black, cures can be obtained without zinc, although admittedly the properties are improved when some soluble zinc is added, Table XVI. The beneficial effects of zinc are most noticeable for carbons with the highest oxygen content. Where the oxygen content is extremely low, as in the case of Shawinigan acetylene black, the effects of zinc are modest. It would seem that the zinc is in some way counteracting the effects of oxygen-containing groups on the surface of the carbon black.

The considerations in this section suggest that part of the active hydrogen of carbon black can be replaced by zinc during vulcanization and that "half-salts"

of zinc containing an accelerator fragment may be formed:



If sulfur combines with carbon black to form thiol groups, these might behave similarly, producing half-salts of the type:



The relative concentration and strength of acidic and basic substances present in the rubber mixture might be expected to be of considerable importance in determining the stabilities of such half-salts. These accelerator fragments might be active or inactive according to the "acidity" of the vulcanization mixture. Stearic and oleic acids, as pointed out by Conant[140], are comparable in strength to acetic acid and surely much stronger acids than hydrogen sulfide, mercaptans and phenols. High oxygen blacks like the color blacks require

TABLE XVI

THE EFFECT OF ZINC LAURATE (LAUREX) CONTENT UPON STRESS–STRAIN PROPERTIES OF CARBON BLACK LOADED–TMTD CURED–NATURAL RUBBER COMPOUNDS [1]

	0 PHR Laurex[2]				3.00 PHR Laurex				20 PHR Laurex			
Carbon Black	Phil-black O	Spher-on 9	Elf O	Acety-lene	Phil-black O	Spher-on 9	Elf O	Acety-lene	Phil-black O	Spher-on 9	Elf O	Acety-lene
300% Modulus (psi)												
Cure 15′ @ 287° F	1200	540	300	1260					1850	1300	1100	2075
30′	980	750	440	1540	1750	1480	1280	1675	1860	1310	1190	2180
45′	1260	1020	680	1490	1825	1460	1125	1560	1860	1425	1250	2030
60′	720	780	480	1260					1960	1380	1225	2080
Tensile Strength (psi)												
15′	3040	2050	1540	2580					3725	3975	4190	3040
30′	2620	2780	1800	2710	3750	3990	4120	3080	3650	3875	4250	2960
45′	2630	2550	1840	2650	3660	3940	3820	3290	3625	3875	4240	2990
60′	2060	2670	2030	2370					3675	3850	4240	2920
% Elongation @ Break												
15′	550	640	680	515					500	600	620	425
30′	550	650	655	490	535	580	630	500	490	565	610	400
45′	505	545	515	450	510	570	615	510	490	550	600	420
60′	580	635	625	500					470	540	600	390
Shore A Hardness												
15′	52	45	48	55					62	63	67	69
30′	50	49	50	55	58	59	59	57	62	62	68	67
45′	52	52	53	57	58	60	60	58	62	63	66	67
60′	48	49	50	55					61	63	66	67

[1] Recipe: Smoked sheets, 100; Carbon black, 50; TMTD, 3.50; Laurex, variable.
[2] For 0 phr Laurex only. All cures between aluminum sheets except 45 minute cures.

surprisingly large quantities of stearic acid to give good cures in MBT-accelerated stocks. It should also be pointed out that sulfur may be able to liberate accelerator fragments from such half-salts. Krebs[141] reports that zinc thiophenolates react with elemental sulfur in the presence of amines to yield zinc sulfide and amorphous polysulfides containing some thiophenol.

G. AN ATTEMPT AT STOICHIOMETRY

Much of our knowledge of the chemistry of vulcanization was obtained by studying the reactions of molecules which are similar to rubber in structure, but of lower molecular weight. Model systems of vulcanized rubber compounds based upon such molecules can be handled in the laboratory by separation and analytical techniques of the organic chemist. A particular advantage of using such mixtures is that with suitable selection of compounding ingredients all, or most, of the mixture can be treated in solution. This permits the use of crystallization, chromatographic separation, distillation, etc. in separating the components for analysis. The success of such methods in studying vulcanization prompted their use in studying reinforcement[77]. The work to date has laregely ignored the liquid portion of the mixture; the carbon black was merely removed from the heated mixture by prolonged extraction with suitable solvents and subjected to precise ultimate analysis.

In formulating these models of filled rubber vulcanizates, squalene was used to replace the chemically analogous molecules of natural rubber. The model compound also contained sulfur, mercaptobenzothiazole (MBT) and commercial zinc laurate (Laurex). After heating at 150° C for one hour, the carbon black was removed by extracting the liquid fraction with toluene, after which it was vacuum dried. The significant changes in composition were:

(1) An increase in hydrogen content, resulting from squalene which could not be removed from the carbon black by prolonged solvent extraction. This increase in hydrogen content was directly proportional to the surface area of the carbon black.

(2) An increase in sulfur content which increased with the product of the surface area of a sample times its hydrogen content. (The oxygen content of the carbon black reduced the amount of sulfur added to the carbon black slightly.)

(3) An increase in nitrogen content of the carbon black which could only have come from the accelerator, MBT.

(4) An increase in zinc content considerably greater than that which could have been present combined with sulfide sulfur.

It was, of course, desirable to extend these studies to cover carbon blacks removed from natural rubber vulcanizates. It was not known how successful the experiments with rubber vulcanizates would be, and the results which have been reported[142] were obtained with almost no background of investigation on the techniques involved. Although future work will, no doubt, utilize improvements in technique, the results obtained so far seem to be of some interest.

The compound chosen for this study was selected to be a simple tetramethylthiuram disulfide (sulfurless) cure of the following composition:

Smoked sheets	100.
Carbon black	50.
TMTD	3.50
Zinc laurate	3.00

The carbon blacks employed were HAF, SAF, EPC, HPC, ACET., LCC types but the samples were not those whose properties are listed in Tables II through VII. Both the zinc laurate and the TMTD and most, if not all, of the latter's decomposition products can be removed from the vulcanizates by extraction with suitable solvents. Zinc dimethyldithiocarbamate is also sufficiently soluble to be removed by prolonged extraction; but zinc sulfide would be expected to remain in the solid fraction, undoubtedly being oxidized by the oxidative degradation used.

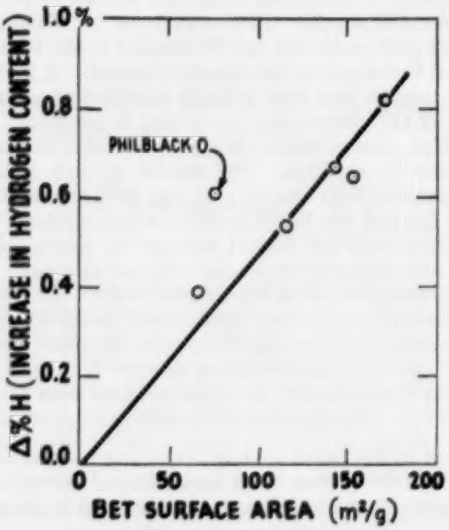


FIG. 32.—The increases in hydrogen contents of carbon blacks removed from natural rubber vulcanizates cured with TMTD are proportional to their surface areas.

In abbreviated form, the technique used involved the following steps:

(1) Swell the vulcanizate at 100° C for 8 hours in *o*-dichlorobenzene.

(2) Increase the temperature and reflux for 48 hours while air is bubbled through the mixture.

(3) After cooling, add 50 ml of *n*-heptane, to aid filtration, and filter through filter paper.

(4) Remove the carbon black which passes through the filter paper, using a Millipore filter.

(5) Combine the two portions of "carbon black" and repeat the *o*-dichlorobenzene digestion with air again bubbled through the mixture. Remove carbon black by filtration.

(6) Repeat (5), giving a total of three 48-hour digestions.

(7) Extract for 30 days with toluene.

(8) Vacuum dry at 150° C for 48 hours (ca. 1 micron final pressure).

(9) Finally, dry in dry nitrogen for one hour at 150° C and analyze for carbon, hydrogen, ash, sulfur, nitrogen and zinc. Sulfide sulfur values must be determined on the undigested vulcanizate because of oxidation during the digestions in *o*-dichlorobenzene.

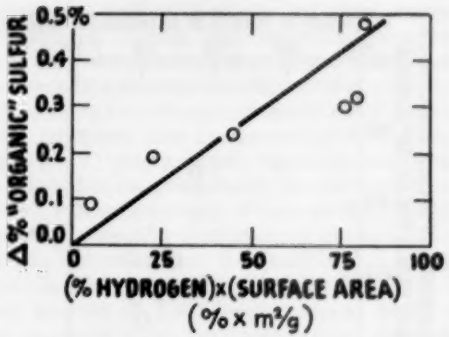


FIG. 33.—Plot of increases in organic sulfur versus (% hydrogen) × (surface area) for carbon blacks removed from natural rubber vulcanizates cured with TMTD.

As was the case in our studies of model systems based on squalene, all samples increased in hydrogen, sulfur, nitrogen and zinc contents, although the amounts differed considerably in the two sets of experiments.

Briefly, the results of this work show:

(1) The increase in hydrogen content is proportional to the surface area of the carbon black, Figure 32. At least two-thirds to three-fourths of the increase in hydrogen content is believed to be due to rubber not removed by the oxidative digestions. Hence, the hydrogen increases indicate that at least two per cent of rubber was not removed from the sample of smallest surface area (acetylene black) and that more than five per cent of rubber was held on the sample of largest surface area (Elf O—see Table 2 for surface area).

(2) The increase in organic sulfur is only roughly proportional to the product of the hydrogen content times the surface area, Figure 33. The scattering

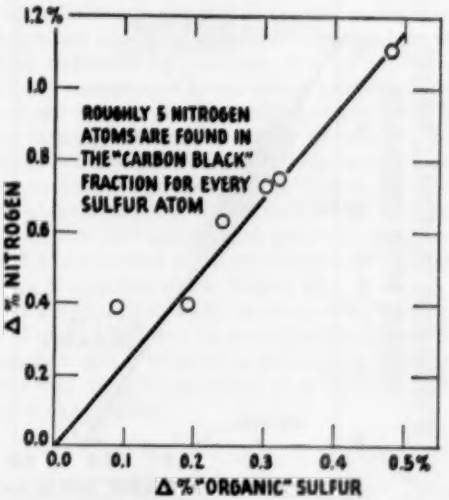


FIG. 34.—Plot showing preferential removal of nitrogen-containing materials by carbon blacks from natural rubber vulcanizates.

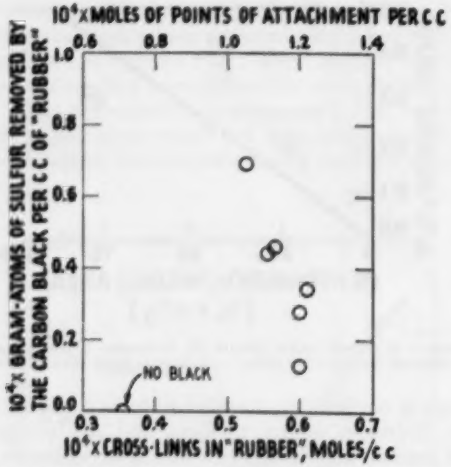


FIG. 35.—Plot showing relationship between the crosslinks found by swelling measurements and the amount of sulfur removed by the carbon black from TMTD cures.

of the data makes it doubtful that this product is the sole or even major factor which determines the increase in organic sulfur of the samples in these TMTD (sulfurless) cures.

(3) The carbons retain nitrogen atoms, roughly five nitrogen atoms for every organic sulfur atom retained, Figure 34. Some of this nitrogen represents nitrogenous material removed from the smoked sheets. This can be deter-

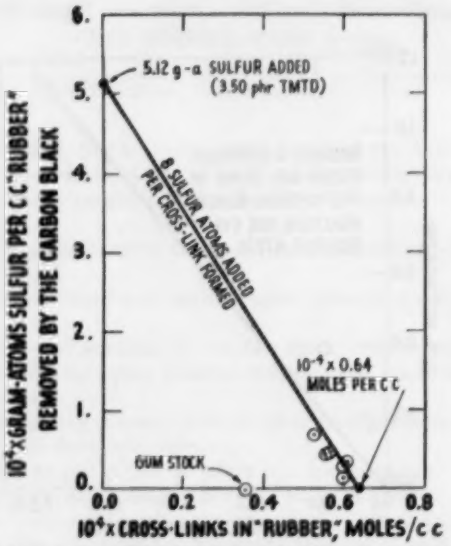


FIG. 36.—Plot showing relationship between the crosslinks found by swelling measurements and the amount of sulfur removed by carbon black from TMTD cures. The TMTD used in this work assayed 50.98% sulfur.

mined by treatment of a carbon black-smoked sheet masterbatch in exactly the same manner (milling, "curing" and removing the carbon black by oxidative degradation in *o*-dichlorobenzene, etc.) as the vulcanizates (cf. Table XI). If the nitrogen contents be corrected by subtraction of a blank determined in this way, there are still roughly two nitrogen atoms retained per organic sulfur atom.

(4) It has been suggested that the formation of the zinc salt of dimethyl dithiocarbamic acid is a necessary step in vulcanization of rubber by TMTD[143]. In the gum stocks considerable amounts of this salt were found, but in the carbon black containing vulcanizates only traces, at most, could be detected. In a few cases no qualitative tests for even traces of the zinc salt could be obtained. This is interpreted as indicating that the ZnDMDC is a by-product of the reactions which take place on curing of gum stocks with TMTD[144]. Further, its absence or virtual absence in TMTD-cured stocks containing carbon black indicates that the reactions which take place during vulcanization are altered by the presence of carbon black so that, at most, only traces of this by-product are formed. It should be pointed out that the zinc content of these stocks was quite low.

(5) In all the stocks containing carbon black, considerably more crosslinks were formed, as measured by Kraus's swelling procedure[7], than were formed in the gum stock.

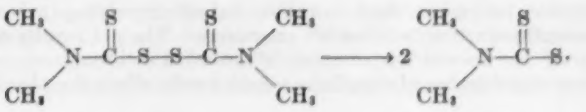
(6) During vulcanization of the carbon black-loaded, TMTD-cured stocks tested, it was necessary to add slightly more than two molecules of TMTD to form one crosslink.

(7) In the presence of the quantities of the carbon blacks used in this study, the reaction conditions appear to be somewhat similar for all rubber-grade carbons, resulting in the relationship described in (6) above. If carbon black is not present, however, considerably more sulfur atoms must be added, as TMTD, to produce one crosslink. (In our gum stock, 14.4 sulfur atoms had to be added to produce one crosslink.) At lower loadings, or with carbon blacks of lower specific surface areas than those used in this study, one might expect values of added sulfur atoms per crosslink formed to be intermediate between those for the carbon black-loaded vulcanizates reported here and the gum stock.

(8) However, as indicated by analyses, the carbon blacks remove sulfur atoms from the rubber matrix, and these cannot participate in the formation of the crosslinks which we measure by the swelling procedure. Each carbon black exhibits a specific capacity to remove sulfur from the rubber matrix. The greater the number of sulfur atoms removed by the carbon black, the fewer crosslinks are found by swelling measurements, cf. Figure 35.

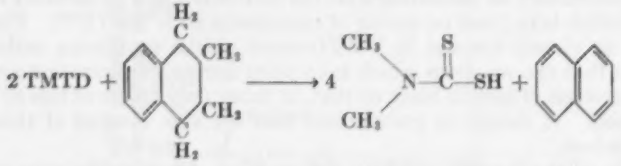
(9) If we add a given amount of sulfur, as TMTD, to a carbon black-loaded stock, in our case 5.12×10^{-4} gram-atom per cc rubber, we can expect very nearly one crosslink to be formed for every eight sulfur atoms which are added but not taken up by the carbon black, Figure 36.

(10) The effects noted in this study, as summarized above, suggest that one important action of carbon black is to promote the dissociation of the TMTD molecules in a manner which is efficient in producing crosslinks. It seems most likely that the first step involves splitting of a TMTD molecule into two dimethyl dithiocarbamyl radicals:



These radicals may then remove hydrogen atoms from the α-methylene carbon atoms forming dimethyl dithiocarbamic acid, an unstable product. The second TMTD molecule must also react to give a crosslink, which, from the evidence obtained so far, contains one sulfur atom.

(11) TMTD is a very effective dehydrogenating agent. In a simple dehydrogenation experiment, TMTD (3.50 parts) was heated in tetralin (100 parts) for one hour at 200° C in a nitrogen atmosphere. 0.72 part naphthalene was formed. Based on a sulfur analysis of the TMTD (50.98% sulfur), this would correspond to a dehydrogenating efficiency of 81%, assuming that each molecule of TMTD can remove two atoms of hydrogen according to the reaction:



When the dehydrogenation was conducted in the presence of Philblack O (50 parts added to the above mixture), only 0.39 part of naphthalene was formed.

It would seem that, in the presence of a strong dehydrogenating agent like TMTD, the carbon black in rubber does not function primarily as a dehydrogenating catalyst, but probably promotes a type of decomposition of the TMTD in a manner which is efficient in producing crosslinks. Certainly we would think from the dehydrogenation results with tetralin that ample dehydrogenating activity is present in the gum stock. And yet, the number of crosslinks formed in the gum stock is considerably less than were formed in the carbon black-containing vulcanizates.

(12) The picture, as presented, cannot be expected to fit all situations. Conditions can be visualized which would be expected to change it. If any TMTD were decomposed prior to curing, as during mixing and storage of the stock under conditions which did not produce crosslinks, or if it were volatilized from the stock during mixing and/or, curing or if some of it decomposed in some way so that crosslinks did not form during cure, then the number of crosslinks would be less than one for every eight sulfur atoms added. It is possible that the small amount of sulfur which forms hydrogen sulfide or zinc sulfide is "wasted" in this way. (It might also be noted that what is measured by the swelling measurements[7] is really the number of network chains. We have assumed that the number of crosslinks is equal to half the network chains so measured. However, this is not strictly true, but may be a sufficiently accurate approximation to be justified in the work reported here.)

H. THE OVERALL PICTURE

In the discussion so far, we have pointed to an intense activity at or in the near vicinity of the carbon black surface. Both chemical and catalytic activity are present although, undoubtedly, the two are in many cases interdependent. The possibilities for carbon black-to-rubber linkages involving carbon-to-carbon and carbon-sulfur-carbon bonding are enormous. The net results point to the possibility of an uneven distribution of crosslinks throughout the sample. Such uneven distribution of crosslinks would surely affect the physical proper-

ties of the rubber. It is considered likely that such "chemical properties" as resistance to oxidation of the sample as indicated by loss in physical properties would be altered by the distribution of crosslinks.

As another link in the picture, experiments were conducted on the rate of removal and analysis of rubber from carbon black in a filled vulcanizate during prolonged oxidative degradation in hot *o*-dichlorobenzene. The rubber sample was first subjected to oxidative degradation in boiling *o*-dichlorobenzene for 96 hours. The carbon black was filtered from the *o*-dichlorobenzene and transferred to a paper thimble. This was placed in a specially designed Soxhlet-type extraction unit in which the vapors of *o*-dichlorobenzene passed around the thimble before entering the condenser. This maintained the temperature at 176 ± 1° C. The solvent was evaporated from the extracted "rubber" at

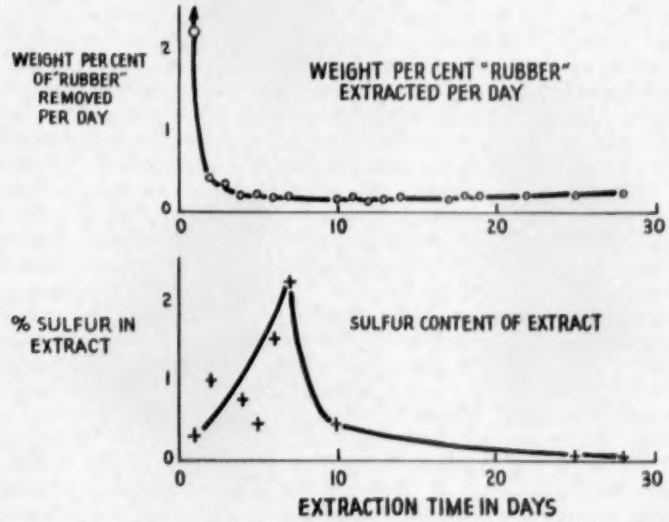


FIG. 37.—Plot showing sulfur content of rubber removed from carbon black stocks by hot o-dichlorobenzene oxidative degradation. The majority of the rubber was first removed by a single 96-hour oxidative digestion and the above data were obtained on the insoluble "carbon black fraction".

intervals of 24 hours in most cases, and the sulfur content of the extract was determined. The amount removed per 24-hour period and the sulfur content of each lot of material removed are shown plotted in Figure 37. The amounts of material available were quite small in the latter part of the treatment, and this made the sulfur analyses somewhat less accurate than was desired; however, the general picture seems clear. Most of the rubber was removed during the first four days; then it was removed at a slow, but nearly constant, rate. Small amounts were still being removed after 28 days. The sulfur content of the material removed passed through a maximum at about seven days. At the end of the 28-day treatment, the amount of sulfur removed was almost negligible. This maximum might be interpreted as indicating that some regions of higher sulfur content exist in the sample. From the curve showing the amount of rubber removed, it is evident that the majority of rubber had been removed by oxidative degradation before the maximum sulfur content was found. These

results have been repeated with a number of other stocks with variations in the details of the extraction procedure. The analyses proceeded to a maximum sulfur content in each case—although displaced on the time scale, apparently because of variations in the technique.

Electron micrographs of normally processed carbon black-loaded rubber vulcanizates almost always show agglomeration of the carbon black particles in the rubber. These agglomerates have been referred to as "islands" or "clouds" by Kruse[145]. They are believed to be present because of the operation of particle-to-particle forces. Bound rubber may well contribute an effect by locking such agglomerates into a structure which persists through processing and vulcanization.

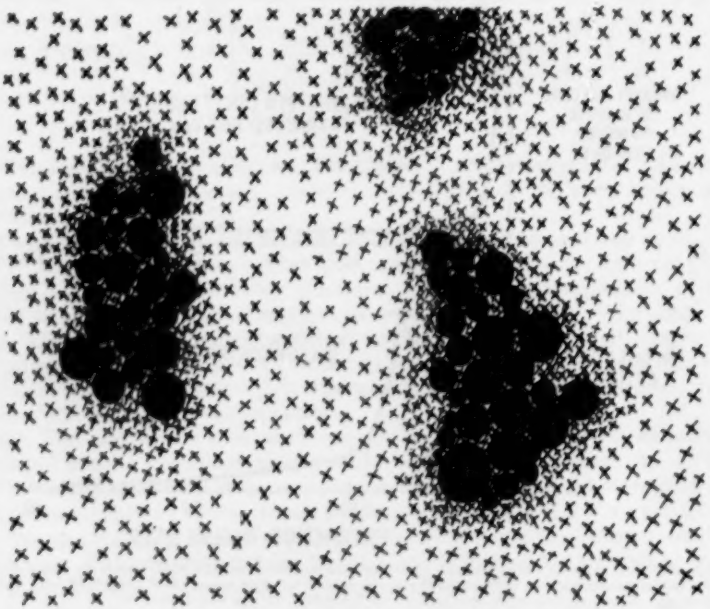


FIG. 38.—Schematic sketch of filled vulcanizate showing agglomerated carbon black particles and uneven distribution of cross-links (x's).

If the intense chemical and catalytic activity at the surface gives rise to an increased crosslinking at or in the near vicinity of the surface, this agglomerated structure will give rise to a three-dimensional network made up of areas in and near the agglomerates of high crosslink density, illustrated schematically in Figure 38. This network would be less readily deformed than the less highly cross-linked rubber matrix. At the loadings normally employed, it is believed that such areas of high crosslink density would extend as a virtual continuum across the sample, being separated by a rubber matrix of lower crosslink density which would more nearly resemble a gum stock with its higher elongation at rupture and its comparative softness.

If this picture is valid, then, to a certain extent, when we impose a stress upon a sample, it will stretch most in the lightly crosslinked matrix between the

islands. Near the break point, the islands, themselves, will deform and break up somewhat. This should certainly alter the shape of the stress-strain curve. Hysteresis properties, tear resistance and abrasion resistance might also be affected. This picture seems consistent with the overall views of Blanchard[3] and Mullins[4,146].

I. SOME PROBLEMS

Throughout this discussion we have tried to picture a chemical and a catalytic activity of carbon black because it is felt that this side of reinforcement has not been given sufficient consideration in the literature. We have barely scratched the surface in this field. The available data are fragmentary, and the subject is fraught with almost endless complications. Yet in spite of this, there seems to be a hint of order.

In presenting the chemical picture, we have ignored the very real physical side of reinforcement. It is hoped that consideration of factors like those presented here will enable physicists and physical chemists to improve their attack on the physical side of the problem. Integration of the chemical and physical studies into a more complete picture of reinforcement is desirable.

It is evident that we cannot divorce the chemistry of reinforcement from the chemistry of vulcanization. Therein lie many of our problems. It would be desirable to be able to answer definitely such questions as the following. What is the point at which the rubber molecule is attacked during vulcanization? Is this point of attack different in the presence of carbon black? Does migration of double bonds take place during vulcanization? Is this migration hindered or promoted by carbon black? How can we determine unequivocally the chemical nature of the crosslinks between rubber molecules? Is it altered by carbon black? What is a sensitive and reliable method for determining unsaturation in the vulcanizates? Is the amount of unsaturation of a filled stock really unchanged during vulcanization? What are the by-products formed during vulcanization? Does the presence of carbon black affect their nature and amount? Are coordination complexes important in vulcanization? If so, how does carbon black affect their nature, stability and properties? Does the choice of accelerator change the answer(s) to these questions? Just how do various carbon blacks react with or alter the reactivity of other compounding ingredients? What is the significance and chemical nature of bound rubber? We could go on and on.

In addition, we may hope to learn much more about the influence of carbon black on oxidative and thermal degradation reactions. The effect of moisture introduced with the carbon black needs more study. Further study of the interaction between rubber, carbon black and other compounding ingredients promises to answer many question for the practical rubber compounder.

The future holds many promises in this fascinating field.

VI. CONCLUSION

In this discussion, we have indicated that carbon blacks display both chemical and catalytic activity which appear to be sufficient to radically alter the chemistry of vulcanization. Much of the chemical reactivity results in removal of molecules or reactive intermediates which might otherwise produce crosslinks. However, in some cases the chemical reactivity seems to be associated with catalytic activity.

When carbon black is heated with rubber, as during hot mixing or during cure, the following types of reaction are considered possible:

a) Alkylation (in a broad sense) of carbon black by rubber molecules. This would be a case of alkylation of an aromatic material by an olefin.

b) Isomerization of the double bond structure of rubber molecules resulting in conjugation.

c) Chemisorption of rubber molecules with dissociation—dehydrogenation—and chemical combination of the rubber-free radicals so formed with the carbon black surface or with themselves, a type of polymerization. Insofar as addition to carbon black is involved, the results of a) and c) are, for practical purposes, identical.

During vulcanization, the action of carbon black will be dependent upon the nature of the rubber, the nature of the curing system and the presence of other compounding ingredients. During cure, carbon black may be considered to act in some, if not all, of the following ways:

1) As a catalyst for dehydrogenation by sulfur.

2) As a catalyst for the oxidation of —SH intermediates to —S—S— crosslinks.

3) As a catalyst to convert polysulfides to disulfides or prevent polysulfide formation. (This particular activity has not been demonstrated; it is suggested in this review only as a possibility.)

4) As a catalyst in activating accelerators by breaking —S—S— linkages, as in TMTD, —S—$(S)_x$—S— linkages in the MBT polysulfide product of Dogadkin and Tutorskiĭ, —S—N— linkages in Santocure, NOBS Special, etc.

5) As a catalyst for hydrogen sulfide formation (associated with 1, above) which is apparently necessary, at least under some conditions, to activate curing systems.

6) As a catalyst in the presence of oxidizing agents for the conversion of hydrogen sulfide (and sulfanes) to sulfur.

7) As a catalyst which promotes a type of decomposition of TMTD, and no doubt other systems, in a manner which is efficient in producing crosslinks.

In the initial phases of vulcanization, its activity as a dehydrogenation catalyst is of considerable importance. This probably involves chemisorption with dissociation of α-methylene hydrogen atoms. This activity directs the chemical reactions of vulcanization to the α-methylene carbon atom and may lead directly to coupling rather than addition reactions at the double bond. After the dehydrogenation step, polymerization reactions, as described in this issue by Craig, should also be considered as possible.

Agglomeration of carbon black particles plus high crosslink density seems to be strongly indicated. This would certainly result in heterogeneous crosslink distribution which would manifest itself in physical properties and possibly in some "chemical properties" of the reinforced vulcanizates.

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